LECTURE-NOTES

ON

CHEMISTRY

FOR

DENTAL STUDENTS
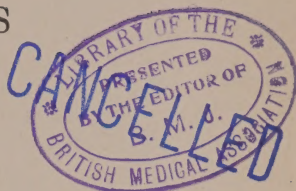
INCLUDING

DENTAL CHEMISTRY OF ALLOYS, AMALGAMS, ETC.

SUCH PORTIONS OF ORGANIC AND PHYSIOLOGICAL CHEMISTRY AS
HAVE PRACTICAL BEARING ON THE SUBJECT OF DENTISTRY

AN INORGANIC QUALITATIVE ANALYSIS WITH SPECIALLY ADAPTED
BLOWPIPE AND MICROSCOPICAL TESTS, AND THE CHEMICAL
EXAMINATION OF URINE AND SALIVA

BY

H. CARLTON SMITH, Ph.G.

LECTURER ON PHYSIOLOGICAL AND DENTAL CHEMISTRY AT HARVARD UNIVERSITY
DENTAL SCHOOL; HONORARY MEMBER OF AMERICAN ACADEMY OF DENTAL
SCIENCE, 1906; OF THE METROPOLITAN SOCIETY OF MASSACHUSETTS
STATE DENTAL ASSOCIATION, 1907; OF HARVARD DENTAL
ALUMNI, 1910; AND NORTHERN OHIO DENTAL
ASSOCIATION, 1912

THIRD EDITION REVISED AND ENLARGED

FIRST THOUSAND

NEW YORK

JOHN WILEY & SONS, Inc.

London: CHAPMAN & HALL, Limited

1917

12 412 123

Copyright, 1906, 1912, 1917,
BY
H. CARLTON SMITH

Stanhope Press
F. H. GILSON COMPANY
BOSTON, U.S.A.

PREFACE TO THIRD EDITION

THREE conditions are responsible for this third edition of a Dental Chemistry: first, the increasing demand for more thorough chemical education for dental students; second, the immense amount of new and valuable material constantly appearing as the result of physiological and dental research; and, third, the apparent demand for a book which shall be of general use to the dental profession aside from its usefulness as a classroom textbook.

In the effort to increase the working value of the book some methods and many references have been included which would be unnecessary if it were designed for school use only.

To facilitate the use of the book in other classes than my own, experiments have been grouped at the end in the belief that a selection may be more easily made from this arrangement than if they were scattered throughout the text.

The outline character of previous editions has been maintained and the student is expected to have access to more complete works, such as those included in the following list, which is strongly recommended and to which frequent references have been made.

Qualitative Analysis . . . . Stieglitz
Qualitative Analysis . . . . Prescott and Johnson
Dental Metallurgy . . . . Hepburn or Essig
Organic Chemistry . . . . Norris
Physiological Chemistry . . . . Hawk, Fifth Edition
Metabolism . . . . Tibbles

References have also been made to current dental literature, not to bring the book strictly up to date, which is practically impossible, but rather to teach the student *how to study*, which is a more important object of any course than mere familiarity with present day theories.

H. C. S.

iii

TO THE STUDENT

As the student of dentistry takes up the study of chemistry, it is necessary that he should realize that the course will be of value to him in the ability acquired to draw correct inferences from observed phenomena, and in the attainment of accuracy and delicacy in manipulation, fully as much as in amount of chemical knowledge obtained. In other words, he must do his own thinking, carry out his own processes and experiments, make his own analyses, or the time spent will be little better than wasted, for the chemical facts which he may happen to remember will be of slight benefit in the work to which every student, worthy of the name, aspires, that of developing, broadening and elevating the profession which he has chosen as his own.

The course of study outlined in this book is designed to furnish the starting-points, which will be of practical value in solving the problems constantly presenting themselves for consideration in the various branches of chemistry. It is hoped that these starting-points may, in the future, serve as the basis for work along the lines of original research and that the best interests of dental science may be furthered thereby.

It is supposed that the student has had the advantage of a laboratory training in general chemistry and is conversant with the properties and methods of preparation of the so-called non-metallic elements, also with the fundamental principles and laws of theoretical and physical chemistry; that he is familiar with laboratory apparatus, such as test-tubes, beakers, crucibles, casseroles, evaporating-dishes, retorts, etc., and that he has had some experience in the ordinary processes of precipitation, filtration, evaporation, distillation, sublimation, and crystallization.

If there is any feeling of insufficient preparation it is strongly advised that a short course of preliminary study be taken. Chemistry furnishes the groundwork of all branches of medical science to a much greater extent than we are apt to think, and even in the study of subjects which in times past have been carried on with little reference to chemistry, we now see the desirability if not the necessity of a good general knowledge of chemical science. The physiologist and the bacteriologist are to-day turning to chemistry for the ultimate solution of their most perplexing problems.

<div align="right">H. C. S.</div>

DIRECTIONS FOR STUDY *

These points carefully followed will enable you to get your lessons more easily, more quickly and to remember them longer than you otherwise would.

(1) Let your lecture notes consist of a very complete, but very briefly stated, list of topics or subject headings concerning which the lecturer has spoken. Then copy and elaborate these topics before the next lecture. Use your topic list as a quiz sheet, asking yourself questions about each one.

(2) Understand the topic — Do not try to remember anything you do not understand. It is a waste of energy and results are of no value to you.

(3) Review often — If you can, study your lesson at two different times, that is, study at night and review it in the morning before going to class. Men who have studied the way in which the mind works, tell us this review helps one to remember.

(4) Concentrate your attention, that is, *keep* your mind on your work, instead of allowing it to wander to the conversation of others or to things happening within sight.

* Taken in part from a sheet of directions by W. C. Crouch.

(5) Study away from interruption. Have a definite place for study where you will not be interrupted.

Regularity of time for study also helps.

(6) Recite and review again. Repeating what you know and reviewing, are the most important factors in mastering any subjects whether a rule in mathematics, a topic in history, or a principle in science. It is a good plan to review hard topics from week to week.
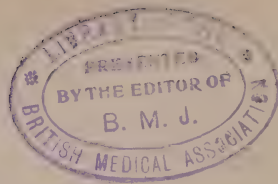
TABLE OF CONTENTS

PART I.

SALTS OF THE METALS AND QUALITATIVE ANALYSIS.

PART II.

DENTAL METALLURGY.

ix

PART III.

VOLUMETRIC ANALYSIS.

PART IV.

MICROCHEMICAL ANALYSIS.

PART V.

ORGANIC CHEMISTRY.

PART VI.

PHYSIOLOGICAL CHEMISTRY.

PART VII.

DIGESTION.

PART VIII.

URINE.

PART IX.

METABOLISM.

DENTAL CHEMISTRY.

PART I.

SALTS OF THE METALS AND QUALITATIVE ANALYSIS.

CHAPTER I.

INTRODUCTION.

EVERY science has a language peculiar to itself, a thorough understanding of which is an essential preliminary to the study of that science. Hence, before we take up the study of Dental Chemistry, it will be well to review a few definitions and perhaps a few of the facts of Physics which are closely related to our subject.

DEFINITIONS.

Matter has been divided into masses, molecules, atoms and electrons, and we are to study first the properties of these divisions. For purposes of present definitions it may be necessary only to consider that aggregations of electrons constitute atoms; groups of atoms make up the molecules; and numbers of molecules held together by the physical force of cohesion form masses. The properties of these divisions of matter will constitute our further definition.

The mass is any quantity of matter which has appreciable weight. It is influenced by such general physical laws as gravitation and adhesion.

The molecule has been defined as the smallest particle of matter that can exist and retain the properties of the original substance, or the smallest particle of matter into which a substance can be divided by physical means. This however gives us no picture of the molecule. To obtain this we must consider the facts of molecular weight, of molecular motion, of intermolecular space and of the effects of heat and cold; then we may be able to see the reasons for some of the things we have already learned about the behavior of chemical substances.

The atoms we will consider as the smallest particles of which the molecule is composed. Our imagination should invest the atoms with all the properties of the molecule, but should include some important differences. First: the *molecules* of a mass are supposed to be all exactly alike in composition. Second: they are attracted to one another in the same way and to the same degree. Third: their separation from one another does not of necessity involve disturbance of the electrical equilibrium of the mass. The *atoms* in the molecule are usually (not always) of different kinds. They are held together by a peculiar force of selective attraction formerly called *chemism* or *chemical affinity;* and electrically considered the uncombined atom is supposed to be either positive or negative.

The electrons are the infinitesimal particles of which the atoms are composed and have been regarded as constituting the force which determines their character. Professor Harry C. Jones says the electrons are negative charges of electricity, and explains their rôle in the theory of dissociation as follows: " Take a salt like potassium chloride. When it is thrown into water an electron passes from the potassium over to the chlorine. The chlorine having received an additional electron thus becomes charged negatively, while the potassium having lost an electron becomes charged positively. If we are dealing with bivalent ions we have simply a transfer of two electrons. Take barium chloride. The barium loses two electrons, one to

each of the chlorines; the latter becoming charged negatively, while the barium has, consequently, two positive charges upon it." The mental picture may be difficult but it is very necessary.

Ions. — The electrically charged particles or parts of molecules capable of attraction to either cathode or anode in the process of electrolysis have been called "ions" (Faraday's definition). Ions may consist of single atoms as in H^+Cl^- or of groups of atoms (radicals) as in water $H^+(OH)^-$ or ammonium hydrate $(NH_4)^+(OH)^-$.

The **molecule** of an **element** consists of but one kind of atoms.

The **molecule** of a **compound** consists of two or more elements chemically combined.

Symbols. — Symbols are used to designate the various elements. In some cases the initial letter of the element alone is used, as C for carbon. In other cases there is added a distinctive small letter of the name when there happen to be a number of elements with names beginning with the same letter such as Calcium, Ca; Cobalt, Co; Copper, Cu; etc.

Chemical Formula. — A chemical formula represents the molecule and is made up of the symbols of the several constituent elements. Chemical formulæ may be empirical, dualistic or graphic. The empirical formula represents the molecule without reference in any way to its structure, i.e., H_2SO_4.

The dualistic formula indicates compounds which may enter into the composition of a molecule. By this sort of formula sulphuric acid would be represented by $H_2O.SO_3$.

The graphic formula attempts to show the probable relation of the atoms in the molecule by means of bonds, e.g.,

$$H-O \diagdown \atop H-O \diagup S \diagup ^O \diagdown _O$$
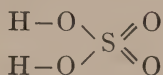
Valence. — Valence is a property of atoms and represents their combining power relative to hydrogen measured, perhaps, by loss or gain of electrons. Valence is not always constant for

the same elements; for example, sulphur has a combining power of six in sulphuric acid, of four in sulphur dioxide and of two in hydrogen sulphide. Nitrogen has a combining power of three in ammonia gas and five in ammonium chloride. Valence has also been indicated by the terms quantivalence and atomicity.

Acid. — An acid is a compound capable of producing upon ionization positive hydrogen ions which may be replaced by a metallic element or radical. The more common acids are sour to the taste and act in characteristic manner upon a number of color compounds known as indicators.

Base. — A base is a substance capable of producing, upon ionization, negative hydroxyl ions which may be replaced by acid radicals. Bases in general characteristics oppose acids. The strongest bases are known as alkalies, e.g., KOH, $NaOH$.

A Salt. — A salt is a substance produced by the chemical union of an acid and a base.

In the formation of the salt the acid may not have been completely neutralized by the base and an *acid salt* results. In such a case the salt contains a part of the hydrogen ions of the acid, e.g., potassium acid sulphate, $KHSO_4$, the production of which may be represented by the equation

$$KOH + H_2SO_4 = KHSO_4 + H_2O.$$

Acid salts may or may not have acid properties such as sour taste and power to give acid reactions with indicators, for example $NaHCO_3$, chemically an acid salt, is alkaline to litmus and has other physical properties of the bases. This fact is explained by the hydrolysis of the salt, hydrolysis being the utilization of the ionized water molecule. The condition may be represented as follows:

$$NaHCO_3 \rightleftarrows Na^+ + HCO^-$$
$$H_2O \leftrightharpoons OH^- + H^+$$
$$\Updownarrow \qquad \Updownarrow$$
$$NaOH \qquad H_2CO_3.$$
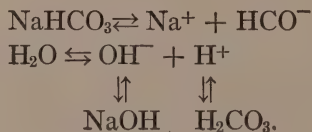
If the acid is exactly neutralized by the base, *neutral salts* result.

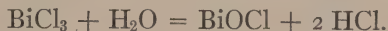$$2 \text{ NaOH} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2 \text{ H}_2\text{O}.$$

A salt may on the other hand be *basic* and contain a portion of the hydroxyl ions (or sometimes oxygen atoms) of the base. Example: $\text{Bi(OH)}_3 + 2 \text{ HNO}_3 = \text{BiOH(NO}_3)_2 + 2 \text{ H}_2\text{O}$ or

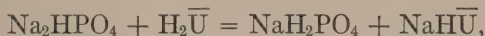$$\text{BiCl}_3 + \text{H}_2\text{O} = \text{BiOCl} + 2 \text{ HCl}.$$

Reactions between chemical substances may be " completed " or " reversible."

A completed reaction is one which progresses in a definite way irrespective of changes in temperature of the quantities of the reacting substances; or, a completed reaction is one in which one of the products is chemically inactive. This inactivity may be due to one of several causes, such as the production of an insoluble precipitate; e.g., AgCl in the reaction,

$$\text{AgNO}_3 + \text{NaCl} = \text{AgCl} + \text{NaNO}_3,$$

or the escape of the product as a gas and its consequent removal from solution — as when carbonates are dissolved by acid.

The reversible reaction is one in which the products remain to a greater or less degree in solution and a change of temperature or increase in quantity of one of the products may start a reverse reaction; for example, at the body temperature, dibasic sodium phosphate and uric acid may become monobasic sodium phosphate and acid sodium urate,

$$\text{Na}_2\text{HPO}_4 + \text{H}_2\overline{\text{U}} = \text{NaH}_2\text{PO}_4 + \text{NaH}\overline{\text{U}},$$

while at reduced temperature,

$$\text{NaH}_2\text{PO}_4 + \text{NaH}\overline{\text{U}} = \text{Na}_2\text{HPO}_4 + \hat{\text{H}}_2\overline{\text{U}}. \quad \text{(See page 242.)}$$
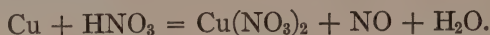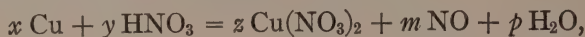
Reversible reactions are expressed by use of the sign $\rightleftarrows$; thus, $\text{MgCl}_2 + 2 \text{ NH}_4\text{OH} \rightleftarrows \text{Mg(OH)}_2 + 2 \text{ NH}_4\text{Cl}$. The reaction may be expressed as an equation if we know what substances take part in the reaction and what products are formed. The

above reaction can be balanced at a glance and is therefore not well suited for illustration but the use of a little more complex equation will show how easily it can be balanced by a few algebraic combinations.

$$Cu + HNO_3 = Cu(NO_3)_2 + NO + H_2O.$$

Represent all these as unknown quantities.

$$x\,Cu + y\,HNO_3 = z\,Cu(NO_3)_2 + m\,NO + p\,H_2O,$$

then

$x\,Cu = z\,Cu$	$x = z$ (1)
$y\,H\ = p\,H_2$	$y = 2\,p$ (2)
$y\,N\ = z\,(N)_2 + m\,N$	$y = 2\,z + m$ (3)
$y\,O_3 = z\,(O_3)_2 + m\,O + p\,O$	$3\,y = 6\,z + m + p$ (4)

(with brace) or

multiplying equation 3 by 3, $3\,y = 6\,z + 3\,m$ (5)

and by elimination (4 and 5), $2\,m = p$ (6)

and $4\,m = 2\,p$, then by eq. 2, $y = 4\,m$ (7)

assuming that $m = 1$, then, in 7, $y = 4$; in 6, $p = 2$; in 3, $2\,z = 3$, or $z = 1\frac{1}{2}$, in 1, $x = 1\frac{1}{2}$. Knowing that all equations must be expressed by whole numbers we double these values and have $x = 3,\ y = 8,\ z = 3,\ m = 2,\ p = 4$.

Upon substituting these values we shall find that the equation "balances."

THEORETICAL CONSIDERATIONS.*

In order to understand the phenomena of solution and precipitation it will be necessary to include in our review a few of the terms of theoretical chemistry such as Phase — Physical Equilibrium — Mass Action — Chemical Equilibrium — Ionization.

The term **Phase** refers to the condition in which a substance exists: solid, gaseous, liquid, crystalline. So sulphur is said to exist in four phases, water in three.

The term **Equilibrium** conveys the idea of equality between

* It is usually desirable that the study of this chapter be accompanied by very thorough lecture room explanations and laboratory demonstration. See

opposing forces resulting in stability, e.g., the water in a closed bottle tends to evaporate; the tension or pressure of the vapor tends to prevent evaporation. When the one force equals the other equilibrium results. Another example, illustrating the meaning of physical equilibrium and at the same time showing why concentration is so often useful in producing precipitates which may be easily filtered, is given by Stieglitz * as follows: " If a crystalline precipitate is in contact with a solvent, e.g., if barium sulphate is in contact with the liquid from which it has been precipitated, then this liquid must be continually in a state of change, not of equilibrium, with respect to the solution and the deposited barium sulphate. The more minute crystals, being a little more soluble than the larger ones, will supersaturate the solution in respect to the larger crystals and the excess will be deposited on these larger crystals and make them grow still larger. This deposition will make the solution unsaturated with respect to the smaller crystals and more of these will dissolve. The process is obviously a continuous one, and must lead in time to the disappearance of the minute crystals and the growth of the larger ones."

Ionization has been defined on page 3, but a further consideration of the subject is necessary if we would understand its effect on chemical reaction. The following important facts have been demonstrated regarding the theory.

The dissociated ions of the molecule are capable of migration and will collect at the poles of a battery according to the well-known laws of magnetic attraction: the positive ion (cation, or metal ion) going to the negative pole, while the negative ion (anion, or acid ion) goes to the positive pole.

Dilution of the solution increases the degree of ionization.

Substances which ionize increase the electrical conductivity of the solution, and the measure of the conductivity is a measure of the degree of ionization.

* Qualitative Chemical Analysis.

A given substance may ionize differently under different conditions, e.g., phosphoric acid may ionize as H^+ and $(H_2PO_4)^-$ or as $H^+.H^+$ and $(H.PO_4)^-$, or as $H^+H^+H^+$ and $(PO_4)^-$. The negative ion of sulphuric acid may be $(HSO_4)^-$ or $(SO_4)^-$. The various atoms of hydrogen of an acid do not ionize with equal facility and the terms primary, secondary, and tertiary ionization may be applied to such cases as the above example of the ionization of phosphoric acid.

The activity of a reagent depends upon the number of free ions in solution.

Reaction between non-ionized molecules takes place very slowly.

Water is the most important ionizing solvent. The alcohols cause less ionization, and the saturated hydrocarbon compounds as Benzene, Chloroform, or Gasolene, very little indeed.

Water itself hydrolyzes to a slight extent and the utilization of the water ions in forming new molecules constitutes "Hydrolysis."

Complex ions may themselves be ionized in the presence of other ionizable compounds.

Mass Action. — The quantity of the reagent has long been recognized as a factor in chemical reaction, e.g., nitric acid will replace hydrochloric acid in combination if the nitric acid is in sufficient excess, or if the hydrochloric acid is in excess the reverse reaction may take place. The completion of a reaction is often impossible without excess of one or the other of the substances involved. The precipitation of insoluble salts depends in many cases upon the quantity of reagent available which in turn may depend upon the degree of ionization.

The application of these facts to the study of the deposition of tartar is one of our present problems.

Chemical Equilibrium. — On page 5 we saw how a certain reagent might act in a given way or the reverse according to the temperature employed. If we couple this idea of chemical

activity with the one given in the preceding paragraph we can easily picture conditions which will result in chemical equilibrium (not inactivity). This has been defined as the point at which two opposite reactions acquire the same velocity.*

SOLUTION AND PRECIPITATION.

"**Solution** is the equal distribution of a body in a liquid, the resulting mass being in all parts homogeneous and fluid enough to form drops," according to an old definition quoted in " Colloids and the Ultramicroscope " by Dr. Richard Zsigmondy.

We can readily adopt this definition for present use provided our conception of homogeneity is sufficiently elastic to include " Colloidal " solutions, and if we remember that the fluidity is not necessarily permanent as we have a number of recognized solid solutions among the alloys. See Chapter XII.

The Law of Partition. — If two immiscible solvents of a given substance are brought together the amount of the substance held in solution by each solvent will be in proportion to the solubility of the substance in each solvent respectively, e.g., $Fe(CyS)_3$ is more soluble in ether than in water, hence in a mixture of water and ether a proportionately larger amount of the salt would be dissolved by the ether.

The solvate theory of solution of Professor H. C. Jones † is briefly, that soluble substances form a large number of definite compounds with the solvent; that the number and complexity of these hydrates diminish as the concentration of the solution increases or as the temperature rises; and that, for the most part the union is between the solvent and the ions, rather than the molecules, of the dissolved substance.

* Jones, " New Era in Chemistry," p. 28.
† This theory is explained in detail in Professor Jones' book " A New Era in Chemistry," Chapter IX.

The colloids are distinguished from crystalloids by their inability to pass through parchment membrane. In colloidal solutions the substance (colloid) may be considered as in suspension or a state of subdivision so nearly complete as to approach closely to the homogeneity of crystalloidal solution.

In many colloidal solutions the particles are large enough to interfere with the passage of light and the preparation is more or less opaque. In some, however, this is not noticeable except by use of polarized light and special apparatus.

There is no sharply defined line between the suspensions and the colloidal solutions, and it is often true that the homogeneity of a solution is dependent upon the " grossness of our means of observation." (Zsigmondy.)

Colloidal substances as a class may be separated from the crystalloids by *Dialysis*, animal membrane suspended in distilled water being used as a separating medium. The crystalloids will pass through the membrane into the pure water, while the colloids remain behind. The use of the dialyzer as applied to saliva analysis is shown on page 316.

Osmosis signifies the passage of water only through a membrane, tending to correct inequalities of pressure produced by differences in molecular concentrations of two solutions.

This is usually illustrated by dropping potassium ferrocyanide solution into copper sulphate. The drop of potassium ferrocyanide becomes surrounded by a film of copper ferrocyanide, through which water alone will pass. Membrane of this character is known as semipermeable.

Porous cups are prepared for demonstrations of osmosis by precipitating within the pores of the cup or cell the ferrocyanide of copper.

Osmotic pressure is the pressure produced within a semipermeable cell by passage of water from the outside; or, as stated by Holland, it is " That push of the molecules of a solute upon its solvent which causes a flow through a membrane into the solution."

Precipitation signifies throwing out of a substance in solid form from solutions. The precipitation may be brought about in three ways:

First, by change of temperature, when the substance precipitated is the same as that previously held in solution;

Second, by change in the character of the solvent, which likewise involves no chemical change and hence, like the first, may be regarded as a physical method.

The *third* method depends upon the formation of a new substance and is, of course, a chemical method.

ILLUSTRATIONS, — *First method:* The separation of crystals of lead chloride by cooling a hot solution of the salt.

Second method: Precipitation of barium chloride from saturated solution by strong hydrochloric acid.

Third method: Any double decomposition resulting in the formation of an insoluble compound.

WEIGHTS AND MEASURES

Measures. — The metric system of weights and measures and the Centigrade thermometer are largely used in all scientific work. The dentist, however, has also considerable use for troy weights and apothecaries' measures if he considers at all the composition of his gold solders, dental alloys, mouth washes, local anesthetics, etc. Hence, a few equivalents are here given.

The *meter* is the primary unit of the metric system and was originally calculated as one ten-millionth part of the quadrant from the equator to the pole.

1 meter = 100 centimeters = 1000 millimeters or 39.37 inches.

1 centimeter = 10/25 or 0.3937 of an inch.

1 cubic centimeter = 16.23 minims or 0.0338 of a fluid ounce.

1000 cubic centimeters (c.c.) = 1 liter or 2.113 pts.

The weight of 1 c.c. of pure water at the temperature of its greatest density (4° C.) is taken as a unit of weight and called a gram (gramme).

1 gram =   15.43 grains.

1000 grams = 1 kilogram (kilo) = 35 oz. 120 grains or 2.2 lbs. avoir.

1 inch = 2.54 centimeters or 25.4 millimeters.

1 oz. av. = 28.3495 grams or 437.5 grains.

1 fluid oz. = 8 fluid drams, 29.57 c.c., or 456 grains of water.

1 fluid dram = 3.7 c.c.

1 troy oz. = 8 drams (℥) or 480 grains.

1 troy oz. = 24 scruples (℈) or 20 pennyweight (pwt. or dwt.).

1 scruple = 20 grains, 1 pennyweight = 24 grains.

1 grain = 64 milligrams.

1 pint = 473.11 c.c.

1 gallon = 8 pints, or 3785 c.c., or 231 cubic inches.

1 lb. avoir. = 7000 grains or 453.59 grams.

Measure of Temperature. — We shall constantly meet reference to both the Centigrade and Fahrenheit scales and an understanding of the relationship of the two methods is essential.

The thermometer is graduated by marking the point at which the mercury stands when the instrument is placed on melting ice; and again the point reached by the mercury when the thermometer is surrounded by dry steam under ordinary atmospheric conditions.

On the Centigrade thermometer, the lower or freezing point is marked zero, the upper or boiling point is marked one hundred, and the intervening space divided into one hundred equal degrees.   On the Fahrenheit scale, these points are marked respectively 32 and 212 and the scale is divided into 180°; hence, 1° C. equals 1.8° or 9/5° Fahrenheit, and 1° F. equals 5/9 of a Centigrade degree.   Providing for the different freezing points

(0° and 32°), we can formulate a rule for converting temperature records from one scale to the other, as follows:

To convert Centigrade to Fahrenheit, take 9/5 of the given number of degrees and add 32.

To convert Fahrenheit to Centigrade, subtract 32 from the given number and take 5/9 of the remainder; e.g.,

$$20° \text{ C.} = 68° \text{ F.}$$
$$-5° \text{ C.} = +23° \text{ F.}$$
$$77° \text{ F.} = 25° \text{ C.}$$
$$14° \text{ F.} = -10° \text{ C.}$$

Absolute Temperature.

According to the Law of Charles or of Gay-Lussac, gases (free molecules) contract 1/273 of their volume, measured at 0° C., for every Centigrade degree that the temperature falls; so it is assumed that, at a point 273° below the Centigrade zero, no further contraction would be possible, molecular motion would cease and all things become solid. This temperature has been called the absolute zero and temperature recorded from this point absolute temperature; thus, water freezes at 273° C. absolute temperature.

GRAVITY.

Specific gravity is the relative weight of equal bulks of different substances, one of which is taken as a standard.

The standard is usually water for liquids and solids.

The standard for gases may be air or hydrogen.

When gases are referred to hydrogen as a standard, the term density is often used instead of specific gravity, and, to avoid confusion, this usage is recommended; i.e., the density of carbon dioxide is 22, while its specific gravity compared with air is about 1.53.

The density of a gas will, according to the Law of Avogadro, be one-half its molecular weight.

The specific gravity of a liquid may be diminished by the solution of a gas, as in case of solution of ammonia; or it may be increased, as in case of solution of hydrochloric acid.

The boiling point of a liquid is raised by the solution of solids, and often by the solution of gases.

CRYOSCOPY.

The freezing point of liquids is lowered by the solution of other substances. As the amount of reduction of temperature necessary to change the liquid to the solid has been found to be in direct proportion to the amount of dissolved substance, it becomes possible to make many valuable determinations by this method. For accurate work, it is necessary to use a special thermometer graduated into hundredths of a degree. The use of the freezing point of a solution in determining the amount of the dissolved substance is known as cryoscopy, and is of great importance in both physical and physiological chemistry.

CHAPTER II.

## THE METALS AND THEIR SALTS.

QUALITATIVE ANALYSIS.

THE metals occur free in nature to quite an extent, but more often combined with other elements. These combinations are chiefly as oxides, sulphides, carbonates and silicates, and in one or more of these four forms the great mass of metals contained in the earth's crust may be found.

Metallic sulphates are found to a considerable extent.

Other natural sources of the metals are phosphates and chlorides, also smaller amounts of nitrates and comparatively slight amounts of bromides, iodides and fluorides. Metals are extracted from their ores chiefly by reduction with some form of carbon. In case of the oxides this reduction takes place directly, according to this reaction: $2 CuO + C = 2 Cu + CO_2$.

In case the metallic combination is a sulphide, the ore is first "roasted" in the air, whereby the sulphur is burned off and an oxide, which may then be reduced as above, is formed:

$$2 CuS + 3 O_2 = 2 CuO + 2 SO_2.$$
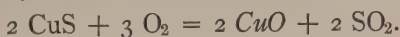
The native carbonates are reduced to oxides by calcination, as

$$CaCO_3 + heat = CaO + CO_2.$$
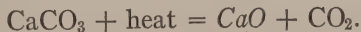
The silicates must first be changed to carbonates by fusion with alkali carbonates; then the reduction may be carried on as before:

$$MgSiO_3 + Na_2CO_3 = MgCO_3 + Na_2SiO_3;$$
$$MgCO_3 + heat = MgO + CO_2.$$
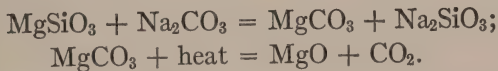
The metals, from certain physical properties, have been variously classified. Thus, in the older books we read of the *Noble*

15

metals, those unaffected by heat, as gold, silver, and platinum; the *Base* metals, such as iron; the *Bastard* metals, those easily crystallizable, as antimony and zinc; the *Metalloids*, sodium and potassium.

As the fact that the properties of metals were to a considerable extent dependent upon conditions of temperature and pressure became better understood, other classifications came to be used, and we may group them according to the chemical behavior of their salts, irrespective of their properties as metals. Thus Ag, Pb, and Hg (mercurous) form a group of metals whose chlorides are insoluble in water or dilute acids. These metals may consequently be thrown out of solution or precipitated by the addition of HCl to any solution of their salts. We therefore let Ag, Hg', and Pb constitute the *First Analytical Group*, and HCl is the *First Group Reagent.*

In like manner we find a group of nine metals that are precipitated from dilute acid solution by hydrosulphuric acid (H_2S). These metals are Cu, Cd, Bi, Hg, As, Sb, Sn, Au, and Pt, and constitute the *Second Analytical Group*, and H_2S is the *Second Group Reagent.*

The fact that the sulphides formed by the first four of these metals are *insoluble* in ammonium sulphide, and those formed by the last five are soluble, furnishes a simple method of separating this group into two parts, *a* and *b*:

Pb,* Cu, Cd, Bi, and Hg constituting Group II (*a*) and As, Sb, Sn, Au, and Pt, Group II (*b*).

Thus, the metals are divided into various analytical groups, each with its own peculiar group reagent. Different groupings are possible, and hardly any two analysts will employ exactly the same scheme for identifying all the metals, although the following group divisions are generally used:

* Lead is included in this group because it is not entirely separated as a chloride in Group I, traces of it remaining in solution even after addition of HCl.

Analytical Groups.

Group I. — Ag, Pb, and Hg′. Metals that form insoluble chlorides and are precipitated from aqueous solution by HCl (the group reagent).

Group II (*a*). — Cu, Cd, Bi, Hg″, and Pb. Metals that form sulphides insoluble in dilute HCl solution and also insoluble in ammonium sulphide.

Group II (*b*). — As, Sb, Sn, Au, and Pt. Metals that form sulphides insoluble in dilute HCl but soluble in yellow ammonium sulphide, or alkaline hydrates.

Group III. — Fe, Al, and Cr. In solutions free from H_2S and which do not contain phosphates, oxalates, tartrates, or salts of certain other organic acids these three metals may be separated by ammonium hydrate (NH_4OH).

Group IV. — Co, Ni, Mn, and Zn. Metals forming sulphides soluble in acid but insoluble in alkaline solution. Ammonium sulphide, $(NH_4)_2S$, is the group reagent.

Group V. — Ba, Sr, Ca, and Mg.* Metals forming carbonates, insoluble in alkaline solutions. The group reagent is ammonium carbonate, $(NH_4)_2CO_3$.

Group VI. — K, Na, Li, NH_4. Metals which cannot be precipitated by any single reagent and for which it is necessary to make individual tests.

It is our purpose to take up the study of the metals according to their analytical grouping: first, the deportment of their salts in solution; later, the metals themselves and their specific application to dentistry.

---

* In the process of analysis, magnesium is held in solution by the presence of NH_4Cl and is not thrown out as a carbonate with the other three members of the group.

CHAPTER III.

METALS OF GROUP I.

Silver, Ag (Argentum).

The Metal. — Atomic weight 107.88. Silver occurs free in masses usually containing gold and copper; as sulphides, such as silver glance (Ag_2S) and in combination with sulphides of antimony, lead, and copper. It also occurs as silver chloride, (AgCl) known as " Horn Silver " or Kerargyrite.

Properties. — Silver fuses at 954° C., forming a revolving globule on charcoal or plaster without oxidation.

At high temperatures, however, silver occludes or absorbs oxygen to the extent of twenty-two times its volume; but as the mass cools the absorbed gas is entirely given off, sometimes resulting in a roughened surface of the metal.

This property may be overcome by alloying with copper or by covering with a considerable layer of common salt.

Silver blackens in the presence of sulphur or hydrogen sulphide. The so-called oxidized silver is a result of heating the metal with a solution of potassium sulphide.

Silver dissolves in hot H_2SO_4 with evolution of SO_2. It is readily soluble in nitric acid with formation of $AgNO_3$, colorless crystals, without water of crystallization.

Silver amalgamates readily, and the " amalgamation process " is one of the important methods for its reduction from the ore.

This process, briefly, is as follows: The ore is roasted with salt, producing chloride of silver; this, in suspension in water, is reduced by metallic iron,

$$2\ AgCl + Fe = FeCl_2 + 2\ Ag.$$

18
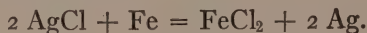
The mixture treated with mercury forms an amalgam from which the mercury can be driven off by heat.

Alloys. — Important alloys of silver are United States coin silver, consisting of silver 90 parts, copper 10 parts; and Sterling silver consisting of silver 92.5 parts, copper 7.5 parts.

Amalgam alloys contain from 50 to 60% of silver, alloyed with tin and slight amounts of other metals such as copper, zinc, and gold. (See page 125.)

A silver platinum alloy used for base plates, clasps, etc., contains from 12 to 35% platinum and is much harder than pure silver.

Von Eckart's alloy,* a French preparation, used for a similar purpose, contains 3.53 parts silver, 2.40 parts platinum, and 11.71 parts copper. Silver solders are alloys of varying proportions of silver, copper, and zinc, the silver running from 60 to 80%.

Compounds. — Salts of silver are liable to decomposition by action of light with reduction in greater or less degree to metallic silver. The salts change from violet to black according to the amount of silver reduced. Such reduction is illustrated in the use of the ordinary photographic plates and paper.

Silver oxide (Ag_2O), a dark brown powder, may be produced in the wet way, i.e., by precipitation of soluble silver salts with hydroxides of the fixed alkalis.

$$2\,AgNO_3 + 2\,NaOH = Ag_2O + H_2O + 2\,NaNO_3.$$

Silver hydroxide (white) may be formed if the above reaction is brought about in alcoholic solution; but it is a very unstable compound, quickly changing to $Ag_2O + H_2O$. Silver thiosulphate, $Ag_2S_2O_3$, may be precipitated white from solution of silver nitrate and sodium thiosulphate. Excess of the thiosulphate produces a soluble double salt $NaAgS_2O_3$. This fact may be utilized in the removal of silver stains.

* Hepburn, page 60.

Fused silver nitrate in the form of pencils or small sticks is used as an escharotic, and is known as " Lunar Caustic." Dilute lunar caustic consists of equal parts of $AgNO_3$ and KNO_3 fused together in pencil form.

Analytical Reactions. — Make the following tests with a weak solution of $AgNO_3$ (about 2%). Write the reactions and enter color and solubility of each precipitate formed in laboratory note-book.*

$AgNO_3$ with HCl gives a white curdy precipitate of AgCl which darkens by action of sunlight. If Ag solution is very dilute, the precipitate will assume the curdy appearance and filter more easily if it is heated and rotated quite rapidly in the test-tube. Allow the precipitate to settle. Decant the liquid carefully, divide precipitate into two parts, and test its solubility in dilute nitric acid, also in ammonia water.

$AgNO_3$ with KBr gives a white precipitate of AgBr, less easily soluble in ammonia than the AgCl.

$AgNO_3$ with KI gives a pale yellow precipitate of AgI, insoluble in ammonia.

$AgNO_3$ with H_2S gives a black precipitate of Ag_2S. $AgNO_3$ with K_2CrO_4 gives a red precipitate of Ag_2CrO_4 in neutral solution. Test the solubility of Ag_2CrO_4 in NH_4OH, HCl, and HNO_3.

Mercury, Hg (Hydrargyrum).

The Metal. — Atomic weight 200.6. Occurs as red sulphide, cinnabar, and in small quantities amalgamated with silver or gold or combined with chlorine or iodine. It is the only metal which is liquid at ordinary temperatures, solidifying at $-39°$ C.

The molecule of mercury consists of a single atom.

* The author uses mimeograph copies of these experiments with space for the reactions and colors of precipitates, which are filled out without reference to the book and handed in by the student at the close of the laboratory exercise.

These reactions have purposely been confined to such as may be applied to the process of analysis.

Properties. — It boils at 360° C. and this wide range of temperature throughout which the fluid form is maintained, together with its comparatively great coefficient of expansion (about 1/160), makes it particularly suitable for use in thermometers and other instruments for measuring temperature or pressure.

At about 270° C. mercury combines with oxygen forming the red mercuric oxide. At the boiling point, it readily leaves other metals, with which it has combined, making the purification by dry distillation a comparatively simple process. The redistilled and chemically pure mercury is usually obtained by distillation in vacuo.

Certain mixtures of metals and mercury act as true chemical compounds forming an exception to the foregoing statement regarding the separation of mercury by heat. (See Chapter XIII, page 119.)

Alloys of mercury are amalgams and will be considered under this head.

Compounds. — Mercury forms two series of salts; one, mercurous, referable to the oxide Hg_2O, in which mercury exhibits a valence of one; and the other, mercuric, referable to HgO, the mercury having a valence of two.

(Mercuric compounds will be considered under group two.)

Mercurous chloride, or calomel, may be made by the reduction of $HgCl_2$ by a reducing agent, as SO_2. $2\,HgCl_2 + 2\,H_2O + SO_2 = 2\,HgCl + H_2SO_4 + 2HCl$; but the process commercially employed is usually to sublime a mixture of mercuric sulphate, sodium chloride and mercury.

$$HgSO_4 + 2\,NaCl + Hg = 2\,HgCl + Na_2SO_4.$$

Mercurous iodide, HgI, is a greenish colored unstable salt produced by double decomposition of $HgNO_3$ and KI.

Mercurous nitrate is an easily soluble salt produced by action of cold nitric acid on excess of mercury, a solution of which may be used for the study of mercurous precipitates.

Note. — The solution of mercurous nitrate, upon standing, will be found to contain more or less mercuric nitrate, unless care is taken to keep excess of mercury in the bottom of the bottle.

Analytical Reactions. — $HgNO_3$ with HCl gives a white precipitate of $HgCl$ (calomel).   After the precipitate has settled, decant the liquid, and test the solubility of the $HgCl$ in ammonia water.   Does it dissolve?   How does its behavior differ from that of $AgCl$?

Alkaline hydroxides form with mercurous salts the black oxide Hg_2O, a preparation of which, made with lime-water and calomel, is known as " black wash."

Lead, Pb (Plumbum).

The Metal. — Atomic weight 207.1.   Occurs as sulphide (Galena), PbS; in lesser quantities as native carbonate (Cerussite); also as phosphate, chromate, and sulphate.

Lead is reduced from the sulphide in a reverberatory furnace by a few simple reactions as follows: $3 PbS + 5 O_2 = 2 PbO + PbSO_4 + 2 SO_2$; then, by increasing the heat without access of air, the sulphur is driven off and the lead separates by two double decompositions,

$$2 PbO + PbS = 3 Pb + SO_2 \text{ and } PbSO_4 + PbS = 2 Pb + 2 SO_2.$$
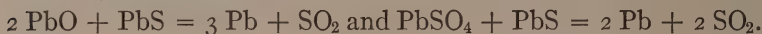
Properties. — Melting-point from 325° to 335° C.   Lead is one of the softest of the metals and can be easily cut with a good knife.   It is a very poor conductor of electricity.

Presence of small quantities of antimony or arsenic tend to harden the metal.*

Lead is very easily separated from its compounds by reduction with carbon.

Lead is soluble in nitric or acetic acid, forming $Pb(NO_3)_2$ or $Pb(C_2H_3O_2)_2$.

Lead is also dissolved to a very slight extent by pure water containing oxygen, or by water containing CO_2, mineral salts, or organic matter.   It tarnishes in the air, with formation of a suboxide, Pb_2O.

* Hepburn, page 137.

Alloys. — Lead forms a large number of important alloys among which are solders and fusible metals as given in Chapter XIV, and type metal which is an alloy of lead and antimony.

Compounds. — Besides the suboxide of lead above mentioned, three more compounds of lead and oxygen are of interest.

Litharge, PbO, is the yellow oxide used in pharmacy as the base of " Diacylon plaster."

The black oxide, PbO_2, is used as an oxidizing agent. Red lead (minium), Pb_3O_4, is practically a mixture of PbO_2 and $2 PbO$, and used as a source of PbO_2 by treatment with HNO_3.

$$Pb_3O_4 + 4\ HNO_3 = PbO_2 + 2\ Pb(NO_3)_2 + 2\ H_2O.$$
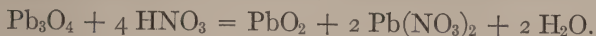
Lead carbonate, as prepared by precipitation of soluble lead salts by alkali carbonates, has the composition $(PbCO_3)_2Pb(OH)_2$.

The basic carbonate, prepared by exposure of the metal to fumes of acetic acid, CO_2, and moisture, is known as " white lead," and is used in manufacture of paint.

Lead acetate, or sugar of lead, formed by solution of the metal or the oxide, PbO, in acetic acid, is a white soluble salt crystallizing with three molecules of H_2O. The solution has an acid reaction to litmus paper.

Lead subacetate, or basic acetate of lead, a solution of which is known as Goulard's extract,* is made by boiling lead acetate solution with litharge. It is used in medicine as an external application and in physiological chemistry as a reagent. It deteriorates by absorption of CO_2 and precipitation of a carbonate.

Lead chromate (chrome yellow) is a yellow insoluble salt used as a pigment.

Lead nitrate, an easily soluble white crystalline salt, may be used in the study of the analytical reactions of lead.

Lead arsenate, a poisonous salt, is quite largely used for spraying trees.

Analytical Reactions. — $Pb(NO_3)_2$ with $2 HCl$ gives white precipitate of $PbCl_2$. Test its solubility in hot water and in NH_4OH.

* Preparation on page 428.

$Pb(NO_3)_2$ with NH_4OH gives white precipitate of $Pb(OH)_2$ insoluble in hot water.

$Pb(NO_3)_2$ with H_2S gives black PbS. Test solubility of precipitate in warm dilute HNO_3.

$Pb(NO_3)_2$ with H_2SO_4 gives white precipitate of $PbSO_4$, forming slowly in dilute solutions.

$Pb(NO_3)_2$ with K_2CrO_4 (or $K_2Cr_2O_7$) gives a yellow precipitate of $PbCrO_4$.

$Pb(NO_3)_2$ gives with KI a yellow precipitate, PbI_2. Avoid excess of the potassium iodide.

By application of the reactions of the salts of Ag, Pb, and Hg', we may formulate a scheme for the separation and identification of the metals of Group I as follows:

Analysis of Group I.
(Ag, Pb, Hg'.)

To the clear solution to be tested add slowly dilute HCl as long as any precipitation occurs. Filter and wash the precipitate *once* with cold water, add this washing to filtrate to be tested for remaining groups, then wash precipitate on the paper with several small portions of *hot* water.
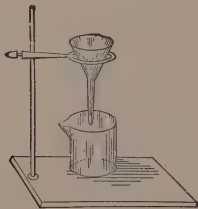

AgCl and HgCl remain undissolved.

$PbCl_2$ is in the hot-water solution.

Divide this hot-water solution into three parts and make three of the following tests for lead: *First*, with $K_2Cr_2O_7$, which gives yellow precipitate of $PbCrO_4$. *Second*, with dilute H_2SO_4, giving a white precipitate of $PbSO_4$. *Third*, with H_2S water, giving black precipitate of PbS. *Fourth*, with KI solution, which forms a yellow precipitate of PbI_2. Write these reactions.

To undissolved residues of Hg and Ag chlorides add warm NH₄OH.
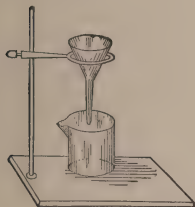
Hg remains on the paper, black, as $Hg + NH_2HgCl$.

Ag is dissolved by the NH₄OH and may be precipitated as AgCl by adding HNO₃ to acid reaction. Presence of Hg in the black residue may be confirmed as in Group II (page 48).

OUTLINE SCHEME FOR ANALYSIS OF GROUP I.

To about one-third of a test-tubeful of the unknown solution add a few drops of HCl.

Ppt. = $AgCl$, $HgCl$, $PbCl_2$. Filter, add hot H_2O.

Residue = AgCl, HgCl. Add NH₄OH.		Solution = PbCl₂. Test as on page 24.
Residue = HgCl. Test, as above.	Solution = AgCl. Test with HNO₃.	

QUESTIONS ON GROUP I.

Why wash the precipitated chlorides only *once* with cold water?

Why is it necessary to wash the lead chloride out with hot water before using ammonia?

Why is ammonia used?

How does nitric acid reprecipitate silver chloride?

Why is it necessary to use two or more confirmatory tests for the presence of lead?

What other metal in group one would give a black precipitate with hydrogen sulphide water?

What precaution must be used in testing for soluble salts of lead with potassium iodide?

CHAPTER IV.

METALS OF GROUP II.

Copper, Cu (Cuprum).

The Metal. — Atomic weight 63.57. Occurs free in vicinity of Lake Superior; also in western United States, Chili, and Spain, as sulphides, copper pyrites, chalcopyrite, $CuFeS_2$; and copper glance, chalcocite, Cu_2S. Malachite green and malachite blue are native basic carbonates of copper.

Properties. — Melting point 1084° C. Copper dissolves easily in nitric acid and with difficulty in hydrochloric acid; heated with sulphuric acid it forms copper sulphate, with the evolution of sulphur dioxide. Copper is second to silver as a conductor of heat and electricity. It expands slightly on solidifying and is corroded by carbon dioxide and moisture forming a green carbonate.

Alloys. — The alloy with mercury, amalgam, was formerly used in dentistry to a considerable extent (page 122). Copper alloys in all proportions with gold, silver, nickel, and zinc. It hardens silver and gold, and is used in the manufacture of coins, jewelry and the solders used in crown and bridge work. Copper is also used in the preparation of bronze, brass, bell metal, dental gold, German silver, Mannheim gold, Mosaic gold, Dutch metal, and Aich's metal. For composition of copper alloys, see page 114.

Compounds. — Salts and solutions of copper are usually blue or green. Copper forms two series of salts: the cuprous, of which there are but few important examples, and the cupric. Cuprous oxide, Cu_2O, which is red in color (sometimes yellow

through admixture of cuprous hydroxide) is obtained by reduction of cupric salts by organic substances such as sugar. Cuprous chloride is used as a reagent for the detection of acetylene gas. Cuprous iodide is a white, insoluble powder used in the preparation of the white copper cements. (See page 138.)

Cupric oxide, CuO, is a black powder formed by ignition of copper in the air or by boiling copper solution with the fixed alkali hydroxides.

Copper arsenate and aceto-arsenite, the latter known as Paris green, are both green powders which have been used as pigments and as insecticides.

Copper sulphate, $CuSO_4$, crystallizes with five molecules of water and is known as bluestone or blue vitriol. It is used extensively in the "Gravity battery," and in copper plating.

Verdigris is a sub-acetate or oxy-acetate of copper; composition, $Cu_2O(C_2H_3O_2)_2$.

Copper salts combine with ammonia, forming a series of "cuprammonium" compounds freely soluble and of intense blue color.

The chloride nitrate and sulphate are the common soluble salts. A 1% solution of either of these will give the analytical reactions.

Analytical Reactions. — $CuSO_4$ with H_2S gives CuS, a brownish-black sulphide. Test its solubility in $(NH_4)_2S$ and in warm dilute NHO_3.

$CuSO_4$ with NH_4OH (one or two drops of reagent) will precipitate $Cu(OH)_2$, bluish white. Add more NH_4OH to the same test-tube and note the result. To this clear solution add a sufficient amount of dry KCN to completely decolorize the liquid. Then add to the mixture some H_2S water. Is the black CuS thrown out? The behavior of Cu solutions thus treated is due to the formation of double salts, the solution in ammonia being due to a compound of $CuSO_4$ and NH_3, and the decolorization of the blue solution to one of $Cu(CN)_2$ and KCN.

CuSO$_4$ with K$_4$FeCy$_6$ (potassium ferrocyanide) gives in acetic acid solution a red-brown precipitate of Cu$_2$FeCy$_6$.

Metallic zinc or iron will precipitate copper from solution. Hold a knife-blade in a solution of CuSO$_4$ for a few seconds.

Mercury in Mercuric Combination.

Compounds of Dyad Mercury. — Mercuric oxide, HgO, is a red powder obtained by ignition of mercury in the air. Mercuric oxide may also be prepared by precipitation of mercuric chloride with alkaline hydroxides. The oxide thus formed is yellow in color, and, when prepared by mixing mercuric chloride and lime water, forms the " yellow wash " used to a considerable extent in pharmacy.

Mercuric chloride, HgCl$_2$. This intensely poisonous salt is known by the fairly descriptive name of corrosive sublimate. It corrodes metals, such as zinc and iron; it coagulates albumin and acts as a corrosive poison when taken internally.

It is made in a manner analogous to that used for the preparation of calomel, i.e., by sublimation, the salts used in this instance being mercuric sulphate and sodium chloride alone.

$$HgSO_4 + 2\,NaCl = HgCl_2 + Na_2SO_4.$$

Mercuric chloride is antiseptic and a disinfectant in dilutions of one to a thousand. Antiseptic tablets designed to give about this strength of solution by the addition of one tablet to one pint of water are made to contain 7.7 grains HgCl$_2$ and 7.3 grains NH$_4$Cl, with sufficient purple coloring to advertise the nature of the tablets and thus act as a safeguard against accidental poisoning. Mercuric chloride is soluble in water and in alcohol. It is used in the preparation of antiseptic gauze, sterile cotton, etc., but, on account of its corrosive properties, cannot be used to sterilize instruments.

Ammoniated mercury, mercur-ammonium chloride or white precipitate (NH$_2$HgCl) is a white powder obtained by slowly pouring a solution of HgCl$_2$ into ammonia water.

Mercuric iodide, red iodide (HgI_2), is made by reaction of mercuric chloride with potassium iodide:

$$HgCl_2 + 2\,KI = 2\,KCl + HgI_2.$$

Mercuric iodide is soluble in excess of either reagent, also in alcohol.

Mercuric iodide combines with potassium iodide (KI) forming an iodo-hydrargyrate, used as a reagent in physiological chemistry (page 406), also as an alkaloidal precipitant.

An alkaline solution of potassium iodo-hydrargyrate constitutes Nessler's reagent, used in analysis of water and of saliva as a test for ammonium compounds.

Analytical Reactions. — A 2% solution of corrosive sublimate ($HgCl_2$) may be used in demonstrating the reactions of dyad mercury.

$HgCl_2$ with H_2S gives first a white precipitate, turning yellow, brown, and finally black, as proportion of H_2S increases. The black precipitate *only* is mercuric sulphide, and care must be taken to add H_2S till this compound is produced.

Test the solubility of HgS in $(NH_4)_2S$ and HNO_3.

To $HgCl_2$ solution add $SnCl_2$. The mercuric chloride is reduced to mercurous chloride (HgCl, white) or metallic mercury (Hg, gray), according to proportions used:

$$2\,HgCl_2 + SnCl_2 = 2\,HgCl + SnCl_4,$$
or $$HgCl_2 + SnCl_2 = Hg + SnCl_4.$$
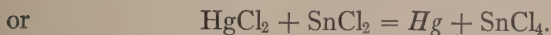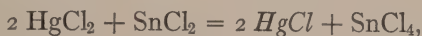
$HgCl_2$ with KI gives red HgI_2, easily soluble in excess of either of the reagents.

$HgCl_2$ with NH_4OH gives white precipitate of $(NH_2Hg)Cl$, known as "white precipitate" (see ammoniated mercury). "Red precipitate" is a term sometimes used to designate the red oxide of mercury, HgO, made in the dry way.

Bismuth, Bi.

The Metal. — Atomic weight 208. Bismuth does not occur in large quantities, but is usually found in the free state. Small amounts are obtained from the oxide, Bi_2O_3, bismuth ochre, and from the sulphide, Bi_2S_3.

It is easily identified by means of the blowpipe test on plaster with S and KI (page 128).

Properties. — Melting-point 268° C. It is a crystalline metal, expands upon cooling and readily unites with oxygen burning with a bluish flame to bismuth oxide. At ordinary temperatures it is brittle and readily dissolved by nitric acid.

Alloys. — The most important alloys from a dental stand-point are the fusible metals, Melotte's metal, Wood's metal, Rose's metal, Newton's alloy, etc. (page 128).

Fletcher states that an amalgam with one part bismuth, fifteen parts tin, and fifteen parts silver, filed and amalgamated with four parts of mercury to one part of the alloy, will adhere to a flat dry surface and may be used as a metallic cement upon apparatus, giving an air-tight joint of great strength.

Compounds. — Salts of bismuth as a rule require excess of acid for permanent solution; and, by adding a considerable volume of water they are easily thrown out of solution as insoluble basic or oxysalts, the reaction of the nitrate being as follows:

$$Bi(NO_3)_3 + H_2O = BiONO_3 + 2\ HNO_3.$$
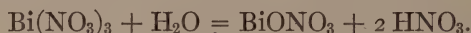
This may be demonstrated by allowing a few drops of bismuth solution to fall into a comparatively large amount of water (two to six ounces). A white cloud of insoluble oxysalt may be observed settling through clear water. This may be employed as a final test for bismuth in the course of systematic analysis.

The subnitrate and the subcarbonate of bismuth are both used in medicine. The latter is a common starting-point in the preparation of other bismuth salts.

Analytical Reactions. — The most available salt is the nitrate, insoluble in water unless strongly acidulated.

Use a 2% solution of $Bi(NO_3)_3$ in the following tests:

$Bi(NO_3)_3$ with NH_4OH gives white precipitate of bismuth hydroxide $Bi(OH)_3$.

$Bi(NO_3)_3$ with H_2S precipitates Bi_2S_3, brownish black, insoluble in $(NH_4)_2S$, but soluble in warm dilute HNO_3.

$Bi(OH)_3$ reacts with sodium stannite (prepared by adding NaOH to $SnCl_2$ till precipitate dissolves) giving a black precipitate of metallic bismuth.

$$4\ NaOH + SnCl_2 = Na_2SnO_2 + 2\ NaCl + 2\ H_2O.$$
$$2\ Bi\ (OH)_3 + 3\ Na_2SnO_2 = 2\ Bi + 3\ Na_2SnO_3 + 3\ H_2O.$$
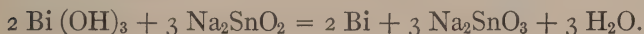
Cadmium, Cd.

The Metal. — Atomic weight 112.4. Occurs associated with zinc in zinc blende. It is more easily volatile than zinc, and advantage is taken of this fact in effecting its separation from that metal.

Properties. — Melting-point 332° C. Cadmium is a comparatively soft metal though harder than zinc or tin. It is usually found in trade in the form of rods which crackle somewhat like tin when bent.

It dissolves slowly in sulphuric acid or hydrochloric acid with the evolution of hydrogen, and easily in nitric acid with the production of nitrogen oxides. It is also soluble in solution of ammonium nitrate, forming cadmium nitrite and ammonium nitrite.

Alloys. — Cadmium is used as a constituent of fusible metals and rarely, in small proportion, in dental alloys. Its use in the latter case is objectionable on account of the production of yellow stain of cadmium sulphide which penetrates the dentine (page 123).

Analytical Reactions. — A 2% solution of the sulphate or nitrate may be used in studying the deportment of cadmium salts.

$CdSO_4$ with H_2S gives a bright yellow sulphide, CdS, soluble in dilute nitric acid.

$CdSO_4$ with $(NH_4)_2S$ also precipitates the yellow sulphide.

Cadmium sulphide forms slowly, and, in presence of Cu or other second-group metals, may escape precipitation if the reagent is added in insufficient quantity.

Arsenic, As.

The Element. — Atomic weight 75.0. Arsenic is on the borderline between the metallic and non-metallic elements, its acid-forming properties predominating. It occurs associated with copper and iron sulphides, as arsenical pyrites, $FeAs.FeS_2$; as native sulphides, orpiment, As_2S_3, and realgar, As_2S_2; also to some extent as the trioxide, As_2O_3.

Compounds. — Arsenic forms two series of salts, the arsenious, As^{III}, and arsenic, As^V, and it also acts as an acid radical forming arsenious and arsenic acids. In the process of analysis, arsenic compounds whether acid or basic are reduced to arsenious by action of hydrogen sulphide. It is most easily obtained in the form of the trioxide, As_2O_3, also known as arsenious acid or white arsenic.

White arsenic is intensely poisonous; but, nevertheless, it has been very freely used in curing the skin of fur-bearing animals and otherwise as a preservative. In dentistry white arsenic is used to devitalize pulp.

Arsenic is widely distributed in nature. It occurs in soft coal from which source it finds its way into the roadside dust and any substance capable of holding dust, such as the majority of fabrics, wall papers, etc. Arsenic is a common impurity in mercury, zinc, and commercial acids. Inasmuch as these things are largely used in the preparation of amalgam and cement

fillings, it is necessary that considerable pains be taken to prevent the presence of the poison in sufficient quantity to cause irritation.

The poisonous character of arsenic differs greatly with the combination in which it occurs. A gaseous hydride of arsenic, AsH_3, being among the most poisonous of its compounds, while some of the organic compounds are claimed to be non-poisonous.

Arsenic forms an insoluble arsenate with ferric hydrate; hence, freshly precipitated ferric hydroxide is the official antidote for arsenical poisoning. This is prepared by mixing 150 c.c. of dilute ferric sulphate solution (containing 50 c.c. of the U.S.P. "Solution") with a well-shaken mixture of 10 grains of oxide of magnesium in about 750 c.c. of water:

$$Fe_2(SO_4)_3 + 3\,Mg(OH)_2 = Fe_2(OH)_6 + 3MgSO_4.$$
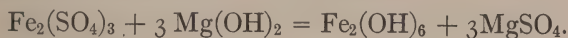
Fowler's solution containing 1% As_2O_3 dissolved by use of potassium bicarbonate; a solution of arsenious acid containing 1% As_2O_3 dissolved by aid of two parts of HCl; Donovan's solution containing 1% each of AsI_3 and HgI_2; and Pearson's solution containing 1% sodium arsenate are Pharmacopœial preparations of arsenic.

Analytical Reactions. — A solution for studying the reactions of arsenic (As^{III}) is conveniently made by dissolving about 15 grams of white arsenic in dilute NaOH solution by aid of heat, then diluting to one liter and acidifying slightly with HCl.

To an arsenious solution, which may be represented by $AsCl_3$, add H_2S water. A lemon-yellow precipitate of As_2S_3 will be thrown down. Test the solubility of this precipitate in yellow ammonium sulphide and in ammonium carbonate.

To the alkaline solution of the sulphide add excess of HCl; As_2S_3 is precipitated.

To an arsenious solution add $(NH_4)_2S$ in repeated small portions.

In neutral solution, as of sodium arsenite, Na_3AsO_3, silver

nitrate will throw down yellow silver arsenite, soluble in excess of nitric acid or ammonia.

SPECIAL TESTS FOR ARSENIC.

REINSCH'S TEST for arsenic, applicable to any solution whether organic or not, and very valuable for a preliminary test, is made as follows: place the solution or mixture to be tested in a porcelain dish, acidify strongly with hydrochloric acid, add a small strip of bright copper foil (cleaned in dilute nitric acid and thoroughly washed in distilled water) and boil for ten or twenty minutes, adding sufficient water to replace loss by evaporation. Remove the copper foil; a dark gray to black coating is an indication of arsenic but not conclusive, as some other substances, mercury and antimony in particular, give similar deposits.

To prove the presence of arsenic, roll the foil as tightly as possible and place it in the bulb of a small glass matrass (Fig. 1).
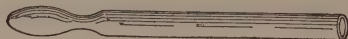
FIG. 1.

Heat the bulb over a very small luminous flame, when tetrahedral or octahedral crystals of arsenious trioxide (As_2O_3) will deposit in the constricted portion of the tube. These may be identified by microscopical examination. There will be sufficient air in the matrass for the formation of the oxide and the test becomes much more delicate than if heated in the ordinary open tube as often recommended.

GUTZEIT'S TEST is made by placing the suspected solution in a test-tube, acidifying with sulphuric acid, adding a few small pieces of arsenic-free zinc, and, as hydrogen begins to be given off, placing over the mouth of the tube a piece of filter-paper carrying a drop of a strong solution of silver nitrate. The presence of arsenic is indicated by the darkening of the moistened filter-paper in accordance with the following reactions:

The nascent hydrogen, liberated by action of the zinc upon the acid, forms with any arsenic present the gaseous arsenious hydride which, in contact with the filter-paper wet with silver nitrate solution, produces a brown or black stain of metallic silver, while the arsenic becomes arsenious acid, H_3AsO_3. The stain may possibly be yellow by formation of a compound of silver *arsenide* and silver nitrate, but, as a rule, moisture is present in sufficient amount to insure the decomposition of this compound.

Antimony will give a similar brown or black stain (not yellow), but the presence of arsenic may be conclusively demonstrated by making FLEITMANN'S TEST, which is conducted in the same way as the preceding, except that the hydrogen is evolved in alkaline solution, either by means of zinc and strong potassium hydroxide solution ($Zn + 2\ KOH = K_2ZnO_2 + H_2$) or by sodium amalgam (made with arsenic-free mercury) and water ($NaHg_x + H_2O = NaOH + Hg + H$). In this case the antimony hydride is *not formed ;* so a stain thus obtained constitutes a positive test for *arsenic*.

MARSH'S TEST for arsenic (or antimony) consists of a simple hydrogen generator with glass tip for burning the gas, as shown in Fig. 2. In this apparatus antimony and arsenic are converted into the gaseous hydrides, arsenic hydride, and antimony hydride; and if a piece of cold porcelain is pressed down upon the flame, arsenic or antimony will be deposited as metallic stains (mirrors) upon the porcelain.

Traces of antimony may be retained in the generator by the introduction of a piece of platinum-foil, the antimony being precipitated

FIG. 2.

upon the platinum to which it adheres quite strongly.

To distinguish between arsenic and antimony spots the following tests will suffice:

Arsenic.	*Antimony.*
Brown-black, lustrous spots.	Dead brown or black surfaces.
Soluble in solution of hypochlorite of lime or soda.	Insoluble in solution of hypochlorite of lime or soda.
Easily volatilized.	Volatilized at red heat.

The Marsh-Berzelius Test for arsenic is the most delicate of all and the one to which we resort in detecting arsenic in the saliva or the urine.   By this method one two-hundredth of a milligram or about 1/12800 of a grain can be easily shown as a brown deposit in the constricted tube at about the point K, Fig. 3.
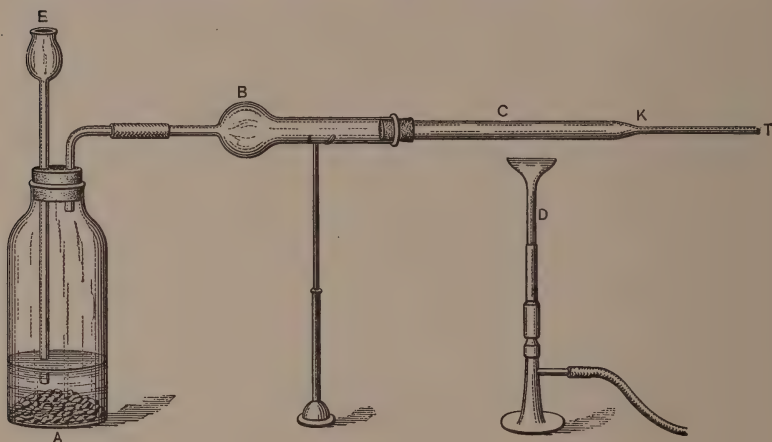
Fig. 3.

The apparatus used in this test is shown in Fig. 3, and consists of a small Erlenmeyer flask, or wide-mouth bottle, fitted as a hydrogen generator, A, and connected with a drying-tube, B, filled with fused calcium chloride, then with a tube of hard glass, C, drawn out to a very small diameter for half its length.

The generator A is charged with arsenic-free zinc, and dilute sulphuric acid (1/5) introduced through the thistle-tube E. After *all air has been driven from the apparatus*, light the escaping hydrogen at T, then the Bunsen burner D, and allow the gen-

erator to run for about twenty minutes, thus making a blank test of apparatus and reagents; if at the end of this time the hard glass is perfectly free from any deposit the suspected liquid, which must have been freed from organic matter (process described in detail in chapter on Urine Analysis), may be introduced in portions of about 10 c.c. each.

The flame should be spread somewhat so as to heat at least one inch of the glass tube. This may be accomplished, in the absence of a burner-tip, by placing an inverted V-shaped piece of asbestos board, one inch wide, over the heated part of the tube.

The presence of arsenic increases the evolution of hydrogen and, unless the solution is added gradually, the arsenious hydride may be driven so rapidly past the flame as to escape decomposition, or the tube may become heated to such an extent that arsenic will not be deposited.

The escape of arsenic at T may be noticed by the bluish color of the flame and by the characteristic garlic odor.

Antimony is similarly deposited as a dead-black stain instead of brown-black, and as antimony is less easily volatile than arsenic the deposit will be nearer the flame, possibly on both sides of it.

FIG. 4.

MERCURIC BROMIDE TEST. — Sanger and Black* have modified the Gutzeit test making the determination of arsenic a quantitative one as follows: The arsenious hydride is passed through a drying tube containing filter-paper (in bulb, Fig. 4) wet with lead acetate
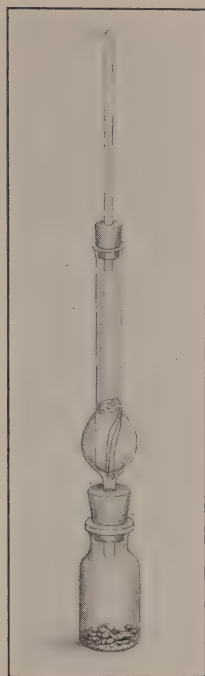
* Proceedings of the American Academy of Arts and Sciences, Vol. XLIII, No. 8, October 1907.

solution to absorb sulphur compounds. Then the gas is passed through absorbent cotton in upper part of drying tube, and then over a paper moistened with mercuric chloride (small tube above drying tube) when the arsenic produces a yellow to brown color on the strip of filter-paper.

The delicacy of this test may be increased by using mercuric bromide in place of mercuric chloride. The process has the advantage of being independent of heat and consequent danger of exploding any mixture of hydrogen and air. The $HgBr_2$ paper is stained yellow to brown beginning at the end next to the generator, and by carefully regulating conditions the extent of the stain may have a quantitative value.

Arsenic compounds (As^V), as Na_2HAsO_4, are of but little interest from the dentist's standpoint.

All arsenic compounds are reduced by nascent hydrogen to arsenious combinations, then to elementary arsenic, then to arsine, (AsH_3), hence the special tests given for arsenious compounds are applicable.

Free chlorine, nitric acid, and potassium ferricyanide oxidize arsenious compounds to arsenic, and in this condition the arsenic is not easily volatilized and organic matter may be destroyed by deflagration (in presence of excess of nitrates) with but slight loss of arsenic.

Antimony, Sb (Stibium).

The Metal. — Atomic weight 120.2. Occurs native in Australia, and as the sulphide Sb_2S_3, known as stibnite or antimonite from which it may be easily reduced by heating with metallic iron according to the following reaction:

$$Sb_2S_3 + 3 Fe = Sb_2 + 3 FeS.$$

Properties. — Brittle crystalline substance volatile at high heat. It ultimately burns to antimonious oxide (Sb_2O_3). Soluble with difficulty in sulphuric or hydrochloric acids.

With nitric acid, antimony acts in a similar manner to tin, forming an oxide which may be antimonious (Sb_2O_3) or antimonic (Sb_2O_5) according to quantity and concentration of acid used (Prescott & Johnson).

Alloys. — Antimony is used in making type metal, Britannia metal, and rarely in low-grade dental alloys.

Compounds. — The salts of antimony may be classified as antimony salts, referable to the hydroxide $Sb(OH)_3$, and antimonyl salts, referable to $SbO(OH)$.

Butter of antimony, antimony trichloride, $SbCl_3$, when pure, is a colorless solid of buttery consistency, hence its name. It may be formed by direct union of constituent elements.

Salts of antimony tend to form oxycompounds and are held in solution by excess of acid. The antimonious chloride $SbCl_3$, in solution with hydrochloric acid is precipitated by excess of water as a white oxychloride $Sb_4Cl_2O_5$, also known as " powder of Algaroth." The antimonic chloride in like manner precipitates the antimonic oxychloride, $SbOCl_3$. Demonstrate by turning 1 or 2 c.c. of $SbCl_3$ solution into a large excess of water.

Tartar emetic, $K(SbO)C_4H_4O_6$, may be prepared by boiling antimony oxide and bitartrate of potassium, filtering and allowing the hot solution to crystallize. It crystallizes with one-half molecule of water.

Analytical Reactions. — A 2% aqueous solution of tartar emetic may be used in the following tests:

To an antimony solution represented by $SbCl_3$ add H_2S water: Sb_2S_3 is precipitated orange-red. Test solubility of the precipitate in $(NH_4)_2S$ and in $(NH_4)_2CO_3$.

How does it differ from arsenic?

Upon the addition of HCl in excess to the ammonium sulphide solution the Sb is reprecipitated, but not necessarily, as Sb_2S_3, but more usually as Sb_2S_5 or a mixture of the two sulphides.

Tin, Sn (Stannum).

The Metal. — Atomic weight 119. Cassiterite, or tin-stone, nearly pure stannic oxide (SnO_2), is by far the most important source. The free metal has been found associated with gold.

Banca tin from the East Indies and block tin from England are pure varieties of the commercial article.

Properties. — Pure tin will give a peculiar crackling sound when bent, due to the crystalline structure of the metal. Tin is very malleable at the ordinary temperature, being fifth in the list of malleable metals (see page 111), but becomes brittle when heated to about 200° C.

Hydrochloric acid dissolves tin slowly, forming stannous or stannic chlorides according to the proportion and temperature of the acid used.

Cold dilute nitric acid will dissolve tin, forming stannous nitrate.

Metallic tin is not dissolved by strong nitric acid, but is converted into a white, insoluble metastannic acid. Hot dilute nitric acid will produce this same result. This acid, upon standing, changes to normal stannic acid which is easily soluble in acids; hence, in making use of this reaction in the analysis of amalgam alloys, it is not well to allow the nitric acid solution of the alloy to stand too long before filtering.

Alloys. — Pewter usually contains Sn, Pb, Cu, and Sb, sometimes Zn. Rees's alloy Sn 20 parts, gold 1 part, and silver 2 parts. Tin is also a constituent of solders, fusible metals, Babbitt's metal, bell metal, and bronze.

An alloy of tin and mercury (tin amalgam) is used for " silvering mirrors."

Compounds. — The salts of tin are not used in medicine but are useful as laboratory reagents.

The chloride ($SnCl_2$) prepared as suggested under properties of the metal is used in solution as a test for mercury.

The stannic salts are the more stable and this solution of stannous chloride easily becomes stannic chloride unless excess of metallic tin is kept in the solution.

Stannous nitrate may be produced by the action of cold nitric acid as follows:

$$4\,Sn + 10\,HNO_3 = 4\,Sn(NO_3)_2 + 3\,H_2O + NH_4NO_3.$$

Tin may act as an acid-forming element in such compounds as sodium stannite (Na_2SnO_2) produced by the solution of stannous hydrate in sodium hydrate,

$$Sn(OH)_2 + 2\,NaOH = Na_2SnO_2 + 2\,H_2O,$$
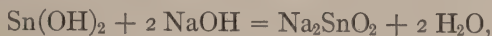
or sodium stannate produced when stannic oxide is fused with sodium hydrate,

$$SnO_2 + 2\,NaOH = Na_2SnO_3 + H_2O.$$

Metallic zinc thrown into a tin solution will precipitate the tin as follows: $SnCl_2 + Zn = ZnCl_2 + Sn.$

This reaction is used in the separation of tin from antimony in the second group; and, in order to obtain the tin in soluble form suitable for a final test, it is necessary to add hydrochloric acid sufficient first to dissolve *all* the zinc present; otherwise it (tin) may remain adhering to the zinc.

Tin, like arsenic and antimony, forms two series of salts, the stannous (Sn^{II}) and the stannic (Sn^{IV}).   A little HCl treated with excess of granulated tin till hydrogen is no longer given off furnishes a solution of stannous chloride suitable for the following experiments:

Analytical Reactions. — $SnCl_2$ with H_2S gives brown precipitate of SnS, soluble in $(NH_4)_2S$, insoluble in $(NH_4)_2CO_3$.

$SnCl_2$ with $HgCl_2$ gives a white or gray precipitate, as explained on page 29 under " Mercury," and is used as a test for presence of mercury.   It may also be used as an alkaloidal precipitant.

Strong solutions of $SnCl_2$ in presence of metallic Sn keep

fairly well, but dilute solutions without an excess of tin oxidize very rapidly to stannic combinations and cease to be of value as reagents.

GOLD, Au (Aurum).

The Metal. — Atomic weight 197.2. It is usually found uncombined, but mixed with various impurities. It occurs frequently as native alloys; of these, two might be mentioned: Calverite, $AuTe_2$, contains 40% gold, and Sylvanite, or graphic tellurium, $(AuAg)Te_2$, contains 24–26% gold.

Gold is extracted from its ores in various ways, the simplest of which is that known as placer mining. This consists of a process of washing out the particles of gold which separate themselves easily because of their heavier weight compared to that of the gravel and stones among which they are found. Hydraulic mining, the utilization of a great force of water to break up the auriferous rock, has come to the aid of placer mining in getting the largest masses ready for the washing process. Other methods are quartz mining in which mercury is used to attract the gold, and the chlorination process.

Properties. — Melting-point 1064° C. Pure gold is a soft metal of yellow color, unless in a very fine state of subdivision produced by the precipitation of the metal when the color varies from purple to brown or nearly black. Gold is more malleable and more ductile than either silver or copper. Gold is second to silver as a conductor of electricity.

Gold is insoluble in simple acids, but may be dissolved in nitrohydrochloric acid (aqua regia) with formation of auric chloride. Gold also unites easily with bromine or iodine, forming $AuBr_3$ or AuI_3.

Gold possesses the property of adhesiveness in a peculiar and very marked degree. By virtue of this the metal can be welded without heat; continued hammering tends to lessen or weaken this property.

When gold-foil is heated to redness (annealed) it recovers the cohesive property which has been largely lost by hammering. The toughness and ductility are also increased. It is recommended that the heating be done in an electric furnace or on plates of mica or platinum, thus insuring uniformity of effect throughout the mass which it is practically impossible to obtain by holding the metal in the flame. See Dental Cosmos, Vol. XLVII, page 233.

Non-cohesive gold, or gold in which the cohesive property cannot be developed by heating, may be prepared by alloying or treatment with carbon. **Corrugated gold** is of this variety and is prepared, according to Essig, by carbonization of unsized paper in intimate contact with the metal. See Essig, Dental Metallurgy, page 173, or Hodgen and Millbury, page 209.

Alloys. — Gold is alloyed with copper to make it harder and more durable for use in the manufacture of jewelry, plate, and coin. It is alloyed with silver for the purpose of reducing its melting-point. Copper and zinc, or copper, silver, and zinc may be used in this way (See page 132 for formulæ for gold alloys.)
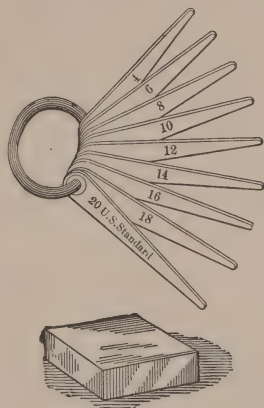
FIG. 5.

The term " carat " * as applied to gold signifies 1/24 part and is used as a measure of purity of an alloy, 22 carat gold being 22/24 pure gold. Twenty carat gold is 20/24 pure, etc. The amount of gold in a given alloy may be determined approximately by use of a device shown in Fig. 5, much used by jewelers, consisting of a series of standard alloys and a piece of stone upon which the test is made. The tips are standard

* The term carat is also used by jewelers as a unit of weight. The legal standard for U. S., since July 1, 1913, has been 200 milligrams.

alloys. Parallel markings are made on the stone with the alloy in question and with the tip supposed to correspond to it; then the addition of a drop of strong nitric acid to the marks and a careful comparison of their appearance will show if the two are of the same composition.

If the composition of an alloy is known, the value in carats may be determined by the following:

Rule to determine the carat of a given alloy: Multiply 24 by the weight of *gold* used and divide result by total weight of alloy. For instance, if an alloy is made containing 9 parts of gold and 3 of another metal, the total weight will be 12 and the calculations $24 \times 9 \div 12 = 18$. The alloy is an 18-carat gold.

Gold may be *raised* to a higher carat by the following rule: Multiply weight of alloy used by difference between *its* carat and that of the metal to be added. Then divide product by the difference between the carat of the metal added and that of the required alloy. The figure thus obtained represents the total weight of *required* alloy. Subtract from this the weight of material taken and the difference is weight of pure or alloyed gold to be added. (From Hall's Dental Chemistry.)

To *reduce* gold to a required carat Essig takes the following rule from Richardson's Mechanical Dentistry: " Multiply the weight of gold used by 24 and divide the product by the required carat. The quotient is the weight of the mass when reduced, from which subtract the weight of the gold used, and the remainder is the weight of the alloy to be added."

Analytical Reactions. — A one-half per cent. solution of $AuCl_3$ may be used in the following tests:

H_2S with $AuCl_3$ gives dark brown Au_2S_3 (auric sulphide), soluble in yellow ammonium sulphide.

Gold is reduced to the metallic state by many of the other metals, as Pb, Cu, Ag, Sn, Al, Sb, Fe, Mg, Zn, and Hg; also by ferrous sulphate, stannous chloride, and oxalic acid.

Add a freshly prepared solution of ferrous sulphate to a little acid solution of $AuCl_3$. Gold is precipitated as follows:

$$AuCl_3 + 3\ FeSO_4 = Au + Fe_2(SO_4)_3 + FeCl_3.$$

Stannous chloride precipitates from gold solution the " purple of Cassius," consisting of a mixture of gold and oxide of tin in colloidal forms.

Gold is only slowly precipitated by oxalic acid; $2\ AuCl_3 + 3\ H_2C_2O_4 = 6\ HCl + 6\ CO_2 + 2\ Au$, but, as Pt is not precipitated at all by this reagent, it is possible to separate Au and Pt in solution of the chlorides, by this means.

KI will give a dark-green precipitate of AuI_2 provided the KI is in excess; if the gold is in excess, the precipitate is apt to be the yellow AuI (aurous iodide). In the presence of a considerable excess of KI the AuI_3 is kept in solution as the potassioauric iodide, $KIAuI_3$. The reduction of this double salt by sodium thiosulphate is made the basis of the method to determine the quantity of Au in a given alloy, as described in the chapter on Volumetric Analysis.

PLATINUM, Pt.

The Metal. — Atomic weight 195.2. Platinum, like gold, is found principally in the free or metallic state, often associated with the rarer metals such as iridium, rhodium, osmium, and palladium; also combined with gold, silver, and copper; a native arsenide, $PtAs_2$ is found in the mineral sperrylite.

Properties. — Melting-point nearly 2000° C. Platinum solubilities are similar to gold; aqua regia forms the chloride $PtCl_4$, or the chloroplatinic acid H_2PtCl_6. Platinum is a white metal unaffected by oxygen, or the fluids of the mouth, hence adapted for use in permanent dental appliances. When melted it absorbs oxygen in a manner similar to silver and when finely divided (platinum black) will absorb or occlude gases to a remarkable degree, one part of platinum black under favorable

conditions absorbing in this way over eight hundred times its volume of oxygen. As this occlusion necessarily means condensation of the gas advantage may be taken of this property to bring about chemical union of gases which will not unite at ordinary temperatures, such as hydrogen and oxygen, oxygen and sulphur dioxide. Platinum black may be made by strong ignition of platinum chloride.

Alloys. — Platinum alloys quite easily with other metals, particularly lead; and platinum utensils may be destroyed by heating in contact with the compounds of metals easily reduced. Sulphur and phosphorus also attack platinum.

Platinum 90% and iridium 10% give an alloy harder, more brittle, and more resistant to chemical action than pure platinum.

Note. — Iridium is a rare metal of particular interest in connection with the platinum alloy given above. Its symbol is Ir; atomic weight is 193.1; melting-point is about 2500° C. It occurs with platinum; also associated with osmium with which it forms a very hard alloy insoluble in aqua regia.

An alloy of platinum and osmium is practically insoluble in acids, is very hard and capable of great expansion. Of the varying proportions of the two metals which may be used those of one to ten per cent. of osmium with ninety to ninety-nine per cent. of platinum prove the most successful. One part of osmium in such an alloy will take the place of two and one half times its weight of irridium.*

" Platinum color," for coloring enamel, is made, according to Mitchell's Dental Chemistry, by precipitating platinum from a solution of $PtCl_4$ by boiling with KOH and grape sugar; then, grinding this finely divided platinum with feldspar in the proportion of one part platinum to sixteen parts feldspar.

Analytical Reactions. — $PtCl_4 + H_2S$ gives a precipitate of sulphide of platinum almost black, soluble in yellow ammonium sulphide.

Platinum solution with NH_4Cl precipitates yellow ammonium

* Hepburn, page 112.

platinic chloride, $(NH_4)_2PtCl_6$, crystalline. Potassium chloride also gives a yellow crystalline precipitate of K_2PtCl_6, isomorphous with the ammonium compound. (Plate III, Figs. 1 and 3.) These reactions may be made quantitative by using neutral, fairly concentrated solutions and adding an equal volume of alcohol.

Both of these double salts are soluble in excess of alkali, and reprecipitated by HCl.

Stannous chloride reduces $PtCl_4$ to $PtCl_2$ but forms no precipitate. Metallic Zn will precipitate platinum as a fine black powder or spongy mass.

Analysis of Group II.

Separation of parts (a) and (b)

A portion of the clear filtrate, from Group I, containing a slight excess of HCl is tested for metals of Group II by the addition of H_2S water.*

If a precipitate is obtained, warm the *whole* of the solution and pass in H_2S gas for from three to five minutes, which precipitates all metals of the group as sulphides. Filter.

Break point of filter-paper with glass rod and wash Group II into beaker with warm $(NH_4)_2S$; digest hot for a few minutes.

Filter and wash the precipitate till wash-water shows only traces of Cl. Throw away all wash-water except the first.
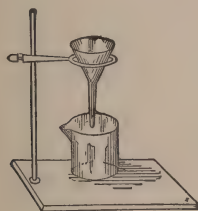
Group II (*a*). Cu, Cd, Bi, Hg, and Pb.

Group II (*b*). As, Sb, Sn, Au, and Pt.

* A preliminary test is made on a part of the solution because in the absence of Group II, the analysis of Group III can be made more easily without the presence of H_2S.

Analysis of Group II (*a*).

Dissolve the precipitate off the paper with hot dilute HNO_3.
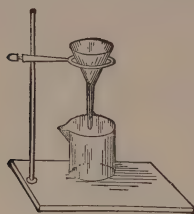
Hg, if present, will remain on paper, black.

Filtrate contains nitrates of Pb, Cu, Cd, and Bi.

Test black residue on paper for Hg^{II} by dissolving in aqua regia and precipitating with $SnCl_2$. For reaction between $SnCl_2$ and $HgCl_2$, see page 29. Aqua regia may be made by mixing two or three parts of HCl with one part of HNO_3. Free Cl is liberated which dissolves the HgS as $HgCl_2$.

$$3\,HCl + HNO_3 = NOCl + 2\,H_2O + Cl_2.$$

If lead is present in Group I, the filtrate above will contain traces which must be separated by adding a few drops of H_2SO_4 and allowing to stand at least fifteen minutes. Filter.
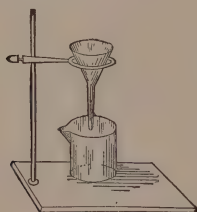
$PbSO_4$ remains on paper.

Filtrate contains Cu, Cd, Bi.

To the filtrate add NH_4OH till alkaline; Bi separates as Bi $(OH)_3$, white. Filter. Confirmatory test for bismuth may be made by pouring over the precipitated $Bi(OH)_3$ on the paper a solution of sodium stannite. If bismuth is present the precipitate turns black in accordance with the reaction given on page 31.

Bi(OH)$_3$.
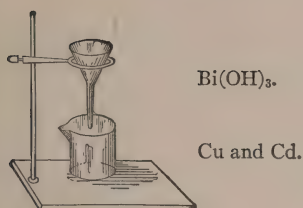
Cu and Cd.

Divide the filtrate (Cu and Cd) into two parts. A blue color indicates presence of Cu. With one part test for Cu by making it acid with acetic acid and adding K$_4$FeCy$_6$, which will give a brown precipitate of Cu$_2$FeCy$_6$. With the other part test for Cd by adding solid KCN very carefully till all blue color has disappeared; then a little H$_2$S water will give a yellow precipitate of CdS if cadmium is present.

Analysis of Group II (*b*).

To the ammonium sulphide solution add HCl till acid. A very fine white precipitate may be sulphur only.

Filter and wash. Throw away wash-water. Pierce paper and wash sulphides into large test-tube or small beaker. Add 10 c.c. of (NH$_4$)$_2$CO$_3$ and heat for a few minutes. Filter.

Sb, Sn, Au, Pt sulphides are on the paper.

Arsenic sulphide is in the filtrate.
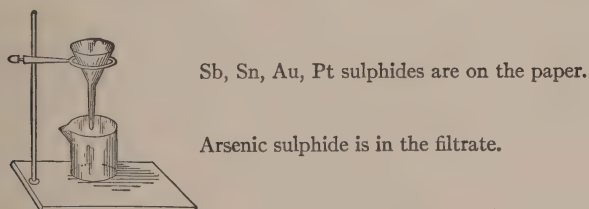
Add HCl and Zn and make Gutzeit's test (page 34) and if necessary Fleitmann's (page 36) or Marsh's (page 35).

Dry this precipitate upon paper and place paper and precipitate in a porcelain evaporator, add concentrated HCl and heat. (This *must* be done under the hood.) Dilute and filter, when Au and Pt will remain undissolved.

Au and Pt.
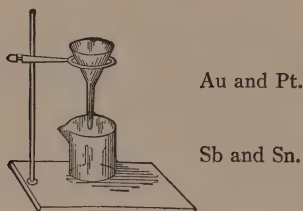
Sb and Sn.

To the Sb and Sn solution add a *little* Zn and a piece of platinum-foil. The antimony and tin will both be reduced to the metallic state, the Sb being deposited on the Pt as a brown or black coating. Presence of Sb may be confirmed by removing the Pt, washing carefully, treating with $(NH_4)_2S$, and drying, when the coating will become Sb_2S_3, orange-red.

To the solution to be tested for Sn add HCl enough to dissolve *all* the Zn which has been added, filter, and test filtrate with $HgCl_2$ (page 29).

Dissolve the insoluble residue of Au and Pt (the residue will be dark-colored if either of these metals are present) in aqua regia and divide solution into two parts.

Test one part for gold with solution of $FeSO_4$, or a mixture of $SnCl_2$ and $SnCl_4$ (page 45).

Test the other part for Pt by adding NH_4Cl, allow to stand over night adding a little alcohol, and a precipitate of ammonium platinic chloride will be obtained, yellow and crystalline (see Plate III, Fig. 1, page 171).

OUTLINE SCHEME FOR ANALYSIS OF GROUP II.

To the warmed filtrate from Group I add H_2S. A ppt. may be sulphides of As, Sb, Sn, Au, Pt, Cu, Cd, Bi, Hg, and Pb.

Filter and treat with warm $(NH_4)_2S$.

Residue is Group II (*a*), page 47, and consists of sulphides of Cu, Cd, Bi, Hg, and Pb. Treat on paper c̄ warm dil. HNO_3.				*Solution* = As, Sb, Sn, Au, and Pt. Reprecipitate c̄ HCl, filter and treat ppt. c̄ strong $(NH_4)_2CO_3$ sol.			
Residue is Hg. Dissolve in aqua regia and test c̄ $SnCl_2$ (page 29).	*Solution* Cu, Cd, Bi, and Pb. Add H_2SO_4 and filter.			*Residue* = Sb, Sn, Au, and Pt, sulphides. Treat c̄ conc. HCl, dilute and filter.			*Solution.* As. Make Gutzeit's or Fleitmann's test for As (pages 34 and 36).
	Ppt. is $PbSO_4$.	*Solution* is Cu, Cd, and Bi. Add NH_4OH and filter.		*Residue.* Au and Pt. Dissolve in aqua regia and divide.		*Solution.* Sb and Sn. Test for Sb c̄ Pt foil and Zn.	
		Ppt. is $Bi(OH)_3$	*Solution* is Cu and Cd.	Part I. Test for Au c̄ $FeSO_4$ (page 45).	Part II. Test for Pt c̄ NH_4Cl and alcohol.	Test for Sn in filtrate c̄ $HgCl_2$ (page 50).	
			Test for Cu c̄ HA and K_4FeCy_6. (page 49.)	Test for Cd c̄ KCN and H_2S.			

QUESTIONS ON GROUP II.

Why is it necessary to wash the precipitate of Group II practically free from Cl before dissolving in warm HNO_3?

How does the Hg found in Group II differ from the Hg in Group I?

Does the Pb found in Group II differ from the Pb in Group I?

Before making the final test for Sn, why is it necessary to dissolve *all* the Zn which has been added?

In precipitating Group II why should the solution be made acid with HCl before adding H_2S?

Why is it better to use H_2S gas rather than H_2S water in precipitating metals of Group II?

Before testing for Cd why add KCN to decolorize the copper solution?

Why is a confirmatory test for bismuth desirable ?

Why must organic matter be destroyed before making Marsh's test for arsenic ?

What reagent would you select for the precipitation of gold and give reason for choice ?

Why is sulphuric acid preferable to hydrochloric in making Marsh's test for arsenic ?

CHAPTER V.

METALS OF GROUP III.

IRON, Fe (Ferrum).

The Metal. — Atomic weight 55.84. Iron occurs widely distributed in nature combined with oxygen as Magnetite or magnetic iron ore, Fe_3O_4; as Red Hematite, Fe_2O_3; or Brown Hematite or Limonite, $2 Fe_2O_3.3 H_2O$; with sulphur as Iron Pyrites or Fool's Gold, FeS_2; and with carbon as Spathic iron ore or Siderite, $FeCO_3$.

The reduction of iron from its ores is typical of one of the four general methods, that is, reduction by carbon. This is carried out in the blast or smelting furnaces, which are so constructed that a supply of coal, iron ore, and suitable flux may be introduced at the top of the furnace. The fusible slag consisting of the flux which has dissolved the impurities of the ore and the purified molten metal is drawn off from the bottom, thus admitting a continuous process. This melted iron, cast in molds as it comes from the furnace, constitutes our cast or pig iron, is brittle, and contains a considerable proportion of carbon, sometimes as much as two and three-tenths per cent., and other impurities.

Wrought iron is produced by working melted iron in specially constructed furnaces so that the greater part of the impurities are removed. It contains less than six-tenths of a per cent. of carbon.

Steel may be made by a more perfect removal of impurities in the Bessemer converter and subsequent mixture of exact proportions of carbon, phosphorus, and manganese. Steel contains from six-tenths to one and six-tenths per cent. of carbon.

Reduced iron or " iron by hydrogen " is prepared by the reduction of the heated oxide or hydroxide in a stream of hydrogen gas, and consists of a very fine powder of pure metallic iron.

Properties. — Melting-point $1275°$ C. Iron dissolves in hydrochloric or sulphuric acid with the evolution of hydrogen. In nitric acid, cold and dilute, ferrous and ammonium nitrates are produced. Warm dilute nitric acid forms ferric nitrate and nitric oxide. Iron is most magnetic of all metals; next in this particular come nickel and cobalt.

Compounds. — Iron forms two classes of salts, ferrous, represented by ferrous sulphate, $FeSO_4$; and ferric, represented by ferric sulphate, $Fe_2 (SO_4)_3$, or ferric chloride, $FeCl_3$.

Ferric sulphate, also known as Monsel's salt, is used as a styptic.

Ferric chloride, $FeCl_3$ or Fe_2Cl_6, is made by dissolving iron in hydrochloric acid, oxidizing the ferrous chloride with nitric acid, and then driving off the nitric acid by evaporation. The resulting solution, however, contains traces of free nitric and considerable free hydrochloric acid. In the tincture of chloride of iron these acids react with the alcohol forming various ethers, to which the peculiarities of the tincture may be due.

Copperas and green vitriol are commercial names for crystallized ferrous sulphate, $FeSO_4.7 H_2O$, which is used as a disinfectant and, to a slight extent, in medicine as an astringent.

Ferrous carbonate, $(FeCO_3)x(Fe(OH)_2)y$, prepared by double decomposition between ferrous sulphate and potassium or sodium carbonate, is a medicinal preparation quite largely used as " Blaud's pills."

Analytical Reactions. — A solution for demonstrating the reactions of ferrous salts is best made by saturating cold dilute sulphuric acid with clean iron wire. A three to five per cent. solution of fresh crystals of ferrous ammonium sulphate may be used. The ordinary ferrous sulphate or " copperas " is almost sure to contain some ferric salt. Use a two to three per cent. solution of

ferric chloride and make the following tests, comparing the deportment of the ferrous and ferric solutions with each reagent. Write the reactions.

H_2S with pure ferrous salts gives no reaction; with ferric salts the iron is reduced to the ferrous combination, but gives no precipitate except sulphur.

$(NH_4)_2S$ gives with ferrous iron a black precipitate of FeS; with ferric salts it gives a precipitate containing FeS and S.

NH_4OH precipitates Fe^{II} as ferrous hydroxide, $Fe(OH)_2$; white if perfectly pure, but usually a dirty green from admixture of ferric compounds. The presence of NH_4Cl prevents a *complete* precipitation as $Fe(OH)_2$.

With ferric salts, NH_4OH completely precipitates the iron as brick-red ferric hydroxide, $Fe(OH)_3$.

K_4FeCy_6 gives with ferrous salts a bluish-white precipitate of potassium ferrous ferrocyanide, $K_2FeFeCy_6$.

With a solution of ferric salts the deep Prussian blue, ferric ferrocyanide, $Fe_4(FeCy_6)_3$, is thrown out.

With potassium ferricyanide, ferrous salts give a dark-blue precipitate of ferrous ferricyanide, $Fe_3(FeCy_6)_2$. With ferric salts no precipitation occurs, but the color may change to green or brown.

KCyS or NH_4CyS gives no reaction with pure ferrous salts, but with ferric salts a deep red solution of ferric thiocyanate, $Fe(CyS)_3$, is produced. This red color is destroyed by addition of $HgCl_2$, not affected by HCl, and may be extracted from the aqueous solution by shaking with ether in which the $Fe(CyS)_3$ is soluble.

ALUMINIUM, Al.

The Metal. — Atomic weight 27.1. Aluminium as a constituent of clay, feldspar, mica, etc., constitutes a considerable part of the earth's crust. The principal sources are Cryolite, Bauxite, and Corundum.

Properties. — Melting-point 657° C. Aluminium is a silver white metal, a good conductor of heat and electricity, and one of the lightest metals, its specific gravity being 2.58. Aluminium is reduced in an electric furnace by the aid of charcoal and copper with which it amalgamates (Cowle's process).

Alloys. — Aluminium alloys are not difficult to produce. The pure metal is used in making plates. A high proportion of aluminium·in alloys is not desirable as it renders the alloy extremely brittle. Alloys containing from five to thirty per cent. are of increasing importance. Aluminium bronze consisting of copper with five to twelve per cent. of aluminium is used as a base for artificial dentures. An alloy used in the preparation of analytical balances and scientific apparatus known as Magnalium contains aluminium and magnesium.

Compounds. — The most important soluble salts of aluminium are ammonia alum, $NH_4Al(SO_4)_2$ 12 H_2O, potash alum, $KAl(SO_4)_2$ 12 H_2O, and aluminium sulphate, $Al_2(SO_4)_3$.

The term alum is applied to any salt of definite crystalline form containing one molecule of a univalent sulphate, such as K_2SO_4 or Na_2SO_4, combined with one molecule of a trivalent sulphate, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$ or $Cr_2(SO_4)_3$, and crystallized with twenty-four molecules of water. The formula of alum, as given above, comprises just one-half of this combination. Alum need not contain any aluminium whatever so long as it conforms to the foregoing requirements, e.g., chrome alum may be $NH_4Cr(SO_4)_2$ 12 H_2O and ferric alum is usually $NH_4Fe(SO_4)_2$ 12 H_2O.

Analytical Reactions. — Use a 5% solution of either of these for the following tests:

$Al_2(SO_4)_3$ with $(NH_4)_2S$ and H_2O gives a white precipitate of $Al(OH)_3$. Write the reaction.

$Al(OH)_3$ is likewise produced by NH_4OH, Na_2CO_3, or $NaOH$; the precipitate is soluble in excess of fixed alkali hydroxides with formation of aluminates:

$$Al(OH)_3 + KOH = KAlO_2 + 2 H_2O.$$
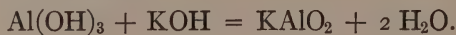
The alkaline peroxides produce aluminates from $Al(OH)_3$. Demonstrate by covering a little precipitated aluminium hydroxide in a porcelain dish with a *very* little water; then sprinkle on to the mixture sodium peroxide in small portions till a clear solution results. Nitric or hydrochloric acid will decompose the aluminate forming again the aluminium salt, which can be reprecipitated by ammonia as $Al(OH)_3$.

The alkaline aluminates may also be formed by fusion with Na_2CO_3 and KNO_3 and then may be dissolved in hot water.

From the solution of $KAlO_2$ the Al may be precipitated as $Al(OH)_3$ by excess of NH_4Cl (difference from Zn, page 66).

The presence of organic acids, tartaric, oxalic, etc., interferes with the precipitation of aluminium hydroxide and may entirely prevent it. The presence of ammonium chloride favors its precipitation.

CHROMIUM, Cr.

The Metal. — Atomic weight 52. Occurs as chrome iron ore or chromite, $FeOCr_2O_3$.

Properties. — Chromium is a hard, grayish colored metal, not used as such in dentistry.

Compounds. — Chromium forms two oxides, one basic in character, Cr_2O_3, which forms the basis of chromic salts, as $Cr_2(SO_4)_3$, $Cr_2Cl_6(CrCl_3)$,* etc.; the other, CrO_3, is an acid anhydride, crystallizes as dark-red needles, and gives rise to two series of salts: neutral chromates, such as K_2CrO_4, and acid chromates or dichromates, $K_2Cr_2O_7$.

Analytical Reactions. — The soluble chromic salts most easily obtained are chrome alum, $KCr(SO_4)_2$, chromic sulphate, $Cr_2(SO_4)_3$, and chromic chloride, $CrCl_3$. With a 5% solution of either of these the following may be demonstrated:

$Cr_2(SO_4)_3$ with $(NH_4)_2S$ gives greenish precipitate of $Cr(OH)_3$.

---

* There is a series of chromous salts, $CrCl_2$, $Cr(OH)_2$, etc., corresponding to a chromous oxide, CrO, but the oxide itself is not known.

Similarly to aluminium, the chromium *hydroxide* is precipitated by the alkaline carbonates and the alkaline sulphides as well as by the hydroxides; and then by boiling the $Cr(OH)_3$ with NaOH or KOH, or by fusing with Na_2CO_3 and KNO_3, or by the action of sodium peroxide and heat, chromates of the alkalis may be produced. The chromate upon the addition of nitric acid becomes the dichromate. This solution after neutralization with ammonia will give a characteristic yellow precipitate of $PbCrO_4$ with soluble salts of lead.

The solid dichromate $K_2Cr_2O_7$ with strong H_2SO_4 gives, in the presence of chlorides, the reddish-brown gas CrO_2Cl_2 (chlorochromic anhydride or chromium dioxychloride) used as a test for chlorides (page 96).

Analysis of Group III.

(Fe, Al, Cr.   Phosphates and oxalates being absent.)

The filtrate from Group II must be freed from H_2S by boiling with a few drops of HNO_3 in a porcelain dish till a drop removed by a glass rod does not blacken filter-paper wet with a solution of lead acetate. This treatment also serves to oxidize the iron (reduced by H_2S) to ferric salt and at the same time concentrates the solution. To the clear solution thus obtained add 10 c.c. of NH_4Cl solution, then NH_4OH till alkaline, when the metals of this group will separate as hydroxides: $Fe(OH)_3$ brick-red, $Al(OH)_3$ white, $Cr(OH)_3$ bluish-green. Filter and wash.
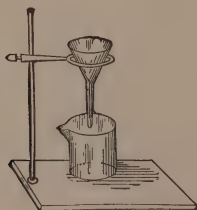
Group III.

Groups IV, V, and VI.

Transfer the precipitated hydroxides to a porcelain dish. Cover with a little water. Add in small portions sodium peroxide not exceeding in total bulk the original precipitate. Add a little more water and boil till oxygen ceases to be evolved, adding water if necessary to keep up the volume of the solution. Filter out iron if it is present.
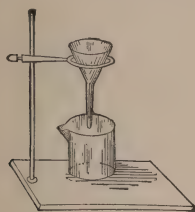
$Fe(OH)_3$.

Al and Cr as negative ions.

Wash the precipitate remaining on the paper (Fe) and dissolve in dilute HCl. Divide resulting solution ($FeCl_3$) into two parts and confirm presence of Fe by testing one with K_4FeCy_6 (blue precipitate) and the other with KCyS (red solution).

If iron is found, determine in original substance whether ferrous or ferric, by use of tests described on page 55.

To the filtrate containing sodium aluminate and chromate add HNO_3 producing $Al(NO_3)_3$ and $Cr_2O_7^=$. Add 5 c.c. of ten per cent. NH_4Cl solution and make alkaline with NH_4OH, which precipitates $Al(OH)_3$. Filter, acidify filtrate with acetic acid and test for presence of chromium with lead acetate solution. (Precipitate is $PbCrO_4$.)

The presence of aluminium may be confirmed as follows:

Transfer the precipitate of aluminium hydroxide to a small evaporating dish, moisten with concentrated nitric acid, add a *very tiny* crystal of cobalt nitrate, and evaporate to dryness. Let the blue flame (O.F.) of the Bunsen burner play directly upon the residue in the dish. Aluminium produces the blue cobalt aluminate.

The aluminium hydroxide should be as nearly white as possible. If it is dark in color, dissolve it in nitric acid and repre-

cipitate with ammonium hydroxide before treating with cobalt, nitrate.*

OUTLINE FOR ANALYSIS OF GROUP III.

Take clear filtrate from Group II and boil with a few drops of HNO_3 to expel H_2S and oxidize Fe''. Add NH_4Cl and NH_4OH and filter.

Ppt. $Al(OH)_3 . Cr(OH)_3 . Fe(OH)_3$. Treat with Na_2O_2. Boil $\bar{c}$ H_2O. Filter (page 58).		*Solution.* Groups IV, V, and VI
Ppt. $Fe(OH)_3$. Test $\bar{c}$ KCNS and K_4Fe $(CN)_6$ (page 59).	Sol. $NaAlO_2$ and Na_2CrO_4. Add $HNO_3 = Al^{+++}$ and $(Cr_2O_7)^=$. Add $NH_4OH = Al(OH)_3$ and $CrO_4^=$. Filter.	
	Test for Al $\bar{c}$ $Co(NO_3)_2$ (page 59).	Test for $CrO_4^=$ $\bar{c}$ $Pb(C_2H_3O_2)_2$

QUESTIONS ON GROUP III.

Why boil off H_2S before precipitating the group with NH_4OH? Why add HNO_3?

In making final test for chromium why is it necessary to acidify with acetic acid?

What is the action of the peroxide of sodium in the separation of aluminium and chromium?

Why is it necessary to test the original solution to determine the character of the iron?

* For the detail of this test as well as for the general method of separation of this group by use of sodium peroxide, the author is indebted to Miss Mary E. Holmes, Associate professor of Chemistry at Mount Holyoke College.

CHAPTER VI.

METALS OF GROUP IV.

Cobalt, Co.

The Metal. — Atomic weight 58.97. Cobalt occurs in nature as an arsenide $CoAs_2$, smaltite; also $CoAsS$, cobaltite. These ores are poisonous and have in times past caused the miners so much trouble that the name cobalt was applied to them, the word meaning, " A demon or mountain sprite." Metallic arsenic has also been called cobalt. These facts are probably responsible for an undeserved reputation which is sometimes attached to the pure oxide of cobalt.

Analytical Reactions. — Use a 2% solution of nitrate. Crystalline salts of cobalt are usually of pink color; anhydrous salts are blue.

$Co(NO_3)_2$ with $(NH_4)_2S$ gives precipitate of cobalt sulphide, black. Test solubility of this precipitate in HCl.

Make a borax bead by fusing a little borax on the looped end of a *clean* platinum wire. When a bead of clear " borax glass " has been obtained, dip it in a little of the cobalt sulphide just formed, and fuse again. The color of the bead when cold is a deep blue.

Note. — Be sure and make the fusion complete; the use of an insufficient amount of heat will account for much of the trouble experienced by students in obtaining satisfactory bead tests.

$Co(NO_3)_2$ with KNO_2 forms a double nitrite, $Co(NO_2)_2$ $2\,KNO_2$, soluble in water; but if sufficient acetic acid is added to produce a strong acid reaction, the solution heated, and then allowed to stand overnight, the cobalt is completely precipitated as another double salt, $Co(NO_2)_2$, $3\,KNO_2$, yellow and crystalline.

Nickel, Ni.

The Metal. — Atomic weight 58.68. It occurs associated with Cobalt, sometimes with Iron or with Copper as a sulphide. Also it is found combined with magnesium as a double silicate called Garnierite, $NiMg(SiO_3)_2.3 H_2O$. Natural alloys of nickel with arsenic and with antimony are to be included among the sources of the metal.

Properties. — The metal is white and hard, and has a high melting-point. It is soluble in dilute mineral acids, most easily in nitric. It is the least malleable of the common metals. It tarnishes very slowly in the air.

Alloys. — The principal alloys are German silver, containing copper, nickel, and zinc, and an alloy of 25% nickel and 75% copper used by the United States Government in making five cent pieces.

In contact with saliva German silver changes rapidly, and in consequence is usually gold plated when used for orthodontia appliances.

Nickel plating. — Nickel is largely used for plating steel and copper. In this process metallic nickel is made the positive pole and substances to be plated are attached to the negative pole of a battery giving not more than five volts. The electrolyte is a solution of nickel and ammonium sulphate made slightly alkaline with ammonia water. Nickel deposits on copper in a much more satisfactory manner than on iron, and from warm solution better than from cold.

The following formulæ are also recommended by Prinz:*

Nickel sulphate......................................	10 parts
Sodium citrate.....................................	9 "
Distilled water	280 "

Nickel and ammonium sulphate........................	70 parts
Boric acid...	25 "
Distilled water.....................................	1000 "

In any case use pure nickel in sheet form as an anode.

* Dental Formulary.

Analytical Reactions. — Use a 2% solution of the sulphate or nitrate. $NiSO_4$ with $(NH_4)_2S$ gives NiS, black. Test solubility in HCl.

The borax-bead test applied to NiS or other nickel salt gives a bead yellowish brown when cold, but the color is easily masked by other metals.

Ni salts with KNO_2 give the soluble double nitrite of similar composition to the Co salt, $Ni(NO_2)_2$, $2 KNO_2$. The nickel salt, unlike the cobalt, is not easily decomposed, and is not precipitated by heating with acetic acid. Advantage is taken of this fact in effecting the separation of cobalt from nickel (page 61).

Manganese, Mn.

The Metal. — Atomic weight 54.93. Occurs chiefly as the dioxide MnO_2, pyrolusite.

Compounds. — The black oxide, manganese dioxide, is commercially important in the production of chlorine. By Weldon's process, the chlorine is obtained from hydrochloric acid, the pyrolusite acting as an oxidizing agent.

The oxidation of manganese dioxide in the presence of potassium hydroxide results in the formation of potassium permanganate, $KMnO_4$. This salt is a valuable disinfectant and is largely used. Its decomposition furnishes five atoms of available oxygen from every double molecule ($K_2Mn_2O_8$).

Condy's fluid, a commercial disinfectant, is a solution of potassium permanganate.

Manganese salts are usually flesh-colored.

Analytical Reactions. — A three per cent. solution of the sulphate may be used in the following tests:

$MnSO_4$ with $(NH_4)_2S$ gives flesh-colored precipitate of MnS. Test solubility in HCl. With a little of the precipitated MnS make a RED-LEAD TEST for Mn as follows:

Place in a test-tube a little red lead (Pb_3O_4). Add three or

four cubic centimeters of a solution of nitric acid (about one part of concentrated HNO_3 and one of H_2O), and boil well. Add, by means of a glass rod, a little of the washed MnS to the mixture in the tube and boil again. Now dilute with water till the tube is about three-quarters full, and allow to stand till liquid is clear. If Mn is present, the supernatant fluid will be a pink to red color due to the formation of permanganic acid, $HMnO_4$.

Note. — HCl or chlorides, even in small quantities, interfere with the reaction; hence it is recommended to make the test on the sulphide. Reducing agents must likewise be absent. When these precautions are observed the test is a very simple and an extremely delicate one.

$MnSO_4$ with NaOH gives flesh-colored $Mn(OH)_2$, insoluble in excess of reagent (separation from Zn).

Upon fusion with a mixture of KNO_3 and Na_2CO_3, manganese salts produce green manganates, as Na_2MnO_4.

ZINC, Zn.

The Metal. — Atomic weight 65.37. Occurs chiefly as the carbonate, $ZnCO_3$, calamine. A native carbonate of zinc is also known as smithsonite. The sulphide ZnS (zinc blende), and the silicate are also natural sources of the metal.

Note. — The name calamine has also been given by Prof. Dana of Yale to a silicate of zinc, $H_2Zn_2SiO_5$.

These ores of zinc, whether sulphide or carbonate, upon roasting in air are converted into oxide, and the oxide is easily reduced by carbon to metallic zinc.

Properties. — Melting-point 420° C. (burns). The metal is bluish white in color, is brittle at ordinary temperatures, but malleable and ductile at 140° to 150° C. At 200° C., however, it again becomes brittle and fuses as above stated at 420° C. At 950° zinc boils and may be distilled; in air it ultimately burns to a white oxide. Whenever zinc ores are sufficiently rich in the metal the pure zinc may be separated by heating with carbon out of contact with the air to a temperature considerably

in excess of its boiling-point, when the zinc distills and may be condensed.

Alloy. — Zinc is of considerable importance from a dental standpoint, the metal itself being used in the manufacture of counter-dies and solders; and, according to Mitchell's Dental Chemistry, it may be advantageously used in the proportion of one to one and five-tenths per cent. in silver-tin amalgam alloys. " It tends to control shrinkage, imparts a ' buttery ' plasticity to the amalgam, adds to the whiteness of the filling and assists in the maintaining of its color." See also page 124.

Compounds. — The oxide of zinc combines with phosphoric acid and is peculiarly adapted to the preparation of dental cements. Zinc salts with alkaline carbonates precipitate a white basic carbonate, $Zn_5 (OH)_6 (CO_3)_2$, which is used as a pigment in the preparation of paint and also as a source of pure oxide of zinc.

The sulphate, $ZnSO_4$, also known as white vitriol, is perhaps the most common salt. The chloride is a constituent of many commercial liquid disinfectants and antiseptics. The nitrate also is easily obtained.

A two or three per cent. solution of any of these soluble salts may be used in the following tests:

Analytical Reactions. — $ZnSO_4$ with $(NH_4)_2S$ gives a white precipitate of ZnS.

Sulphide of zinc is the only white *sulphide* formed in the course of analysis of ordinary solutions, but the following white precipitates are formed: Sulphide of manganese is flesh-colored or dirty white. Aluminium hydroxide resembles sulphide of zinc in appearance and is precipitated by $(NH_4)_2S$. Yellow $(NH_4)_2S$ added to an acid solution will precipitate sulphur, white, very fine and difficult to filter out.

$ZnSO_4$ with NaOH (or KOH) gives a white gelatinous precipitate of zinc hydrate, $Zn(OH)_2$, soluble in excess of the reagent as Na_2ZnO_2 (sodium zincate).

Note. — Colorless gelatinous precipitates in slight amounts may escape detection, as it sometimes takes careful observation to see them, especially if the laboratory light happens to be poor.

Na_2ZnO_2 with H_2S or $(NH_4)_2S$ gives precipitate of ZnS.

From solution of Na_2ZnO_2 the Zn may be precipitated as $Zn(OH)_2$ by addition of NH_4Cl, but further addition of the NH_4Cl redissolves the precipitate (distinction from Al, page 57).

$ZnSO_4$ with K_4FeCy_6 gives white precipitate of zinc ferrocyanide (Zn_2FeCy_6), insoluble in NH_4OH.

Note. — The ferrocyanide and the sulphide are the only two zinc salts not soluble in NH_4OH. (Prescott and Johnson, page 179.)

Soluble zinc salts, with oxalic acid or oxalates, give a precipitate of zinc oxalate sufficiently insoluble in alcohol and water to make it available for use in the quantitative separation of zinc from dental alloys. The crystals are of characteristic form, which may be recognized under a microscope (Plate II, Fig. 6, page 170).

Analysis of Group IV.
(Co, Ni, Mn, Zn.)

(In the presence of phosphates, oxalates, borates, etc., examine this group by the scheme given on page 88.)

To the clear filtrate from Group III add $(NH_4)_2S$. A precipitate may be NiS,* CoS, MnS, and ZnS. Wash the precipitate and treat with *cold dilute* HCl, which will dissolve MnS and ZnS only.
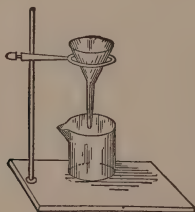
CoS and NiS, black.

$MnCl_2$ and $ZnCl_2$ in solution.

* A black precipitate persistently passing through the paper is NiS, and sometimes requires heating or concentrating before a clear filtrate can be obtained.

Make a borax-bead test (page 61) of the precipitates on funnel in above figure. If a clear red-brown bead is obtained, Ni alone is present. If the bead is blue, Co is present, Ni may or may not be.

Separation of Cobalt and Nickel.

If Co is present, dissolve the black precipitate off the paper with aqua regia, evaporate in porcelain capsule practically to dryness, dissolve in H_2O, add excess of acetic acid and potassium nitrite (KNO_2). Allow to stand over night, when Co will separate out as a yellow crystalline precipitate (page 61).

Filter and test filtrate for Ni with NaOH, which gives a pale-green precipitate of $Ni(OH)_2$ insoluble in excess of the precipitant.

Separation of Manganese and Zinc.

Boil the HCl solution of Zn and Mn to expel the H_2S, then add a decided excess of KOH or NaOH and allow to stand ten minutes *without* heating. Mn will separate out as $Mn(OH)_2$, while Zn will remain in solution as K_2ZnO_2.

$Mn(OH)_2$.

K_2ZnO_2.
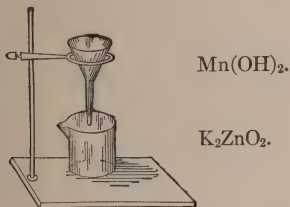
Test precipitate by the red-lead test for Mn, page 63. Test filtrate for Zn by adding H_2S or a few drops of $(NH_4)_2S$, which will precipitate ZnS, white.

OUTLINE FOR ANALYSIS OF GROUP IV.

To filtrate from Group III add $(NH_4)_2$ S.   Filter.

Ppt.$=$CoS, NiS, ZnS, MnS.   Treat c̄ dil. HCl.

Residue. Co and Ni. Make borax bead test. Separate Co by means of KNO_2 (page 61)	Sol. Mn and Zn. Boil and heat c̄ KOH or NaOH.
	Ppt. Mn(OH)$_2$. Make red-lead test	Sol. K_2ZnO_2. Add $H_2S =$ ppt. ZnS (page 67)

QUESTIONS ON GROUP IV.

Why dissolve the MnS and ZnS in *cold* and *dilute* HCl?

Why is it necessary to separate *all* the Mn before testing for Zn?

If traces of Co or Ni are dissolved by the HCl, how does it affect the final test for Zn?

In this analysis (in absence of phosphates, etc.) what important difference between the behavior of salts of Zn and Al?

Why is it necessary to allow time for *complete* precipitation of Co with KNO_2?

Why expel H_2S before separating Mn?

Where does this H_2S come from?

CHAPTER VII.

METALS OF GROUP V.

The Alkaline Earths Ba, Sr, Ca, Mg.

The common alkaline earth metals present similarity of properties which ally them more closely than the metals of some of the previous analytical groups. None of the metals occur free in nature. The metals themselves are isolated with considerable difficulty, with the exception of magnesium, and they all decompose water with evolution of hydrogen; calcium, strontium, and barium producing the decomposition at ordinary temperatures; magnesium, at high temperatures only.

As a group they form insoluble carbonates, from which carbon dioxide is easily driven off by heat, leaving the oxide of the metal. This oxide unites with water, forming feebly soluble hydroxides. The solutions of the hydroxides are alkaline to litmus, and are used, to a considerable extent, in medicine, as antacids.

There are two other metals belonging to this group. The first, glucinum, also called beryllium, has an atomic weight of 9.1. Soluble salts of glucinum are precipitated by ammonium hydroxide as white and gelatinous beryllium hydroxide. The precipitate somewhat resembles aluminium hydroxide. Ammonium carbonate also precipitates the hydroxide, which is easily soluble in excess of reagent. The solution, however, should not be boiled as prolonged boiling will cause the beryllium hydroxide to reprecipitate.

Beryllium oxide unites with phosphoric acid, forming a phosphate similar in its properties to the basic phosphate of zinc, and its use is claimed by some manufacturers to be essential to the preparation of artificial enamels. (See page 138.)

69

The second rare metal belonging to this group is radium; atomic weight 226.4. The metal itself has not as yet been isolated. Its compounds are obtained from uraninite or pitchblende, a source of uranium. It is bivalent, and the chlorides, bromides, nitrates, and hydroxides have been studied.

Radium compounds are luminous, and the active emanations emitted by them have been condensed at 150° below zero centigrade, forming new substances, among which helium has been identified. The discovery of this fact is responsible for our new conception of the divisibility or disintegration of what were once considered indivisible atoms, also of the " smoke ring " molecule, and the possible transmutation of the elements.

Barium, Ba.

Compounds. — Barium, the next metal to radium in this group in point of atomic weight, which is 137.37, occurs chiefly as a sulphate $BaSO_4$, heavy spar, and $BaCO_3$, witherite. Barium oxide may be formed by heating the carbonate or nitrate to red heat. It absorbs oxygen from the air with formation of the binoxide BaO_2. This in turn is decomposed, oxygen being given off and BaO being reproduced. The barium oxide hence becomes a source of oxygen of commercial importance. The cost of producing oxygen by this method is obviously small.

The peroxide of barium is also of particular importance to the dentist, in that it is an important source of peroxide of hydrogen. This substance is considered more fully in a chapter on mouth washes and local anesthetics. (See page 180.)

Barium hydroxide, BaO_2H_2, slightly soluble in water, absorbs CO_2 very rapidly and may be used as a test for this gas. The solution is known as " Baryta Water."

Analytical Reactions. — Use a 2% solution of the chloride for tests.

$BaCl_2$ with $(NH_4)_2CO_3$ gives white precipitate of barium

carbonate. Test solubility in acids. With soluble sulphates $BaCl_2$ produces $BaSO_4$ insoluble in HCl. (Test for sulphates.)

$BaCl_2$ with $K_2Cr_2O_7$ or K_2CrO_4 gives yellow precipitate of $BaCrO_4$. Barium salts moistened with HCl and held on a clean platinum wire give to the colorless flame of the Bunsen burner a green or yellowish-green color.

STRONTIUM, Sr.

Atomic weight 87.63. Occurs as the carbonate, $SrCO_3$, strontianite, also as the sulphate.

Strontium salts are used commercially in the preparation of colored fires, strontium imparting a vivid red color to the flame. Strontium oxalate crystallizes in practically the same forms and much more easily than calcium oxalate.

Analytical Reactions. — Use a 3 to 4% solution of the nitrate or chloride for tests.

$Sr(NO_3)_2$ with $(NH_4)_2CO_3$ gives white precipitate of $SrCO_3$.

$Sr(NO_3)_2$ with H_2SO_4 or soluble sulphate gives white precipitate of $SrSO_4$, rather more soluble in water and more slowly formed than $BaSO_4$.

A saturated solution of $SrSO_4$ may be used to test for barium in presence of Sr salts.

$Sr(NO_3)_2$ with K_2CrO_4 gives precipitate of $SrCrO_4$, but with the acid chromate (dichromate) of potassium, $K_2Cr_2O_7$, no precipitate is formed except in concentrated solutions.

$Sr(NO_3)_2$ with oxalic acid gives a precipitate of strontium oxalate, SrC_2O_4, crystallizing in the so-called envelop form (Plate II, Fig. 3, page 170). Salts of Sr color the Bunsen flame crimson.

CALCIUM, Ca.

Atomic weight 40.07. Calcium is widely distributed and very abundant, limestone, chalk, marble, and calc-spar being natural carbonates; $CaCO_3$, gypsum, and alabaster are sulphates.

Calcium phosphate occurs in the mineral apatite and is also a principal constituent of animal bones.

Plaster of Paris. — Calcium sulphate is of particular interest, occurring as gypsum, $CaSO_4.2 H_2O$. Upon heating, the two molecules of water of crystallization may be driven off, leaving the anhydrous $CaSO_4$, or plaster of Paris, so largely used in dental laboratories. If the heat used is too high a "dead burnt" plaster results which unites so slowly with water as to be practically useless. More careful dehydration at a lower temperature yields a so-called "soluble anhydrite" which absorbs water rapidly. The best plaster for dental purposes is neither of these, but a product which contains one molecule of water to every two of calcium sulphate. This is known as the half hydrate and is the chief constituent of plaster of Paris. This half hydrate has a property of setting with more or less of a fibrous character which permits its use in the formation of plaster casts. Essig states that if, in the preparation of plaster, the heat is allowed to exceed 127° C., its affinity for water is impaired or destroyed and this effect will not be produced.*

As plaster sets, more or less expansion takes place, and, if spread upon glass, the mass usually rises slightly in the center, producing a plate which is somewhat concave on the under surface. This tendency to expansion varies with different grades of plaster, as may easily be shown by a method suggested by Dr. George H. Wilson in the Dental Cosmos for August, 1905, page 940, which consists simply of filling small glass beakers with mixtures similarly prepared. Some samples were found to expand so slightly as not to injure the glass, others cracked, and some broke the beaker into fragments.

In the Dental Cosmos for 1908, page 67, Dr. J. H. Prothero of Chicago shows that plaster during the first four minutes gives a slight contraction, and is then stationary for about forty-five seconds. Then it expands with increasing rapidity till the maxi-

* American Text-book of Prosthetic Dentistry.

mum movement attained is one-thousandth of an inch per minute for about ten minutes. After half an hour the movement practically ceases. The slightest possible trace of potassium sulphate added to the water used in mixing and the least possible agitation reduces both the rate and the amount of expansion.

The method of mixing also affects the amount of expansion. In a valuable article on "Experiments in Plaster of Paris to Test Expansions," by Dr. Stewart J. Spence, in Items of Interest, 1902, page 721, it is shown that "not only do different plasters expand in differing degrees, but the same plaster expands very differently according to the stirring given it before pouring," and that long stirring increases the heat developed, the rapidity of setting, and the amount of expansion, but decreases the strength.

Various methods have been prepared to overcome the difficulties in manipulation of plaster, such as mixing the plaster with alum, marble-dust, or potassium sulphate. A compound on the market consists of a mixture of plaster and Portland cement. A mixture which has been very strongly recommended as an investment preparation consists of two-thirds plaster and one-third powdered pumice-stone.

Analytical Reactions. — Use a 3 or 4% solution of $CaCl_2$ for tests.

$CaCl_2$ with $(NH_4)_2CO_3$ gives white precipitate of $CaCO_3$, easily soluble in acids.

$CaCl_2$ with oxalic acid or soluble oxalates gives a white precipitate of CaC_2O_4, similar in form to the SrC_2O_4 but much more difficult to obtain in the crystalline condition.

$CaSO_4$ is not precipitated except from moderately concentrated solution.

A saturated solution of $CaSO_4$ may be used to test for strontium salts in presence of Ca.

Magnesium, Mg.

The Metal. — Atomic weight 24.32. Principal sources are the carbonate, $MgCO_3$, magnesite, and a double carbonate, $CaMg(CO_3)_2$, dolomite. The sulphate $MgSO_4$ occurs in the mineral kieserite in the "Stassfurt deposit." "French chalk" (or talcum), soapstone, and meerschaum consist of magnesium silicate in varying states of purity.

Asbestos is a double silicate of magnesium and calcium.

Properties. — Magnesium is a silver white metal occurring in trade as ribbon or powder. It burns easily in air, forming MgO and traces of Mg_3N_2 and producing a white light which is used in photography. It is a light metal having a specific gravity of 1.75.

Alloys. — For the alloy with aluminium, see page 56. The amalgam alloys are not practical as they heat and swell in a manner which renders them practically useless.

Compounds. — Epsom salt, or magnesium sulphate, occurs as a constituent of laxative waters. The crystallized salt, $MgSO_4.7 H_2O$ resembles oxalic acid in appearance, and has been mistaken in several instances for the poisonous acid.

Magnesium carbonate is used in pharmacy in two forms; viz., the light and the heavy. These are produced by precipitating dilute or concentrated solution of magnesium sulphate with sodium carbonate.

The light and heavy magnesium oxides are produced by calcination of the light or heavy carbonates. Magnesium salts are quite generally distributed in the human system, but in small quantities. They occur in the bones, the teeth, and the various body fluids.

Analytical Reactions. — A five per cent. solution of the sulphate or nitrate may be used in the following tests:

Magnesium salts with $(NH_4)_2CO_3$ give a white precipitate of basic carbonate of variable composition. This precipitate

forms *very* slowly in dilute solution, and in the presence of NH_4Cl the formation of soluble double salts prevents the precipitation altogether.

$MgCl_2$ with Na_2HPO_4 gives in fairly concentrated solution a white precipitate of $MgHPO_4$. In presence of NH_4Cl and NH_4OH the alkaline phosphates precipitate magnesium-ammonium-phosphate, $MgNH_4PO_4.6\,H_2O$, even from *very* dilute solution (Plate IV, Fig. 2).

In case the precipitate has formed very slowly, it may separate as small, almost transparent, crystals clinging to the sides of the beaker.

Ammonium oxalate does not precipitate magnesium solutions.

Analysis of Group V.

(Ba, Sr, Ca, Mg.)

To the filtrate from Group IV containing NH_4Cl and NH_4OH, add $(NH_4)_2CO_3$. (If NH_4Cl and NH_4OH are not present, add 10 c.c. of NH_4Cl solution and NH_4OH till strongly alkaline before proceeding with the analysis.) Ba, Sr, and Ca will be precipitated as carbonates; Mg will be held in solution by the ammonium chloride. Filter.
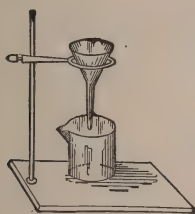
Ca, Ba, Sr carbonates.

Mg and metals of Group VI.

Test the filtrate for Mg by adding Na_2HPO_4, when a white crystalline precipitate is $NH_4MgPO_4.6\,H_2O$.

To the carbonates on the paper add dilute acetic acid, which will dissolve the precipitate, forming acetates of the three metals.

Take a *portion* of the acetate solution in a test-tube and make a preliminary test for Ba by adding *acid* chromate of potassium ($K_2Cr_2O_7$). A yellowish precipitate will be $BaCrO_4$.

If *Ba is present*, add $K_2Cr_2O_7$ to the whole of the solution and filter out the $BaCrO_4$.
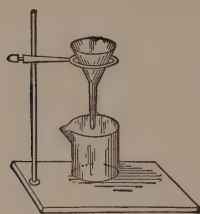
$BaCrO_4$.

Sr and Ca acetates, $K_2Cr_2O_7$, etc.

It is desirable to remove the excess of bichromate from the filtrate before testing for Ca and Sr.* To do this add NH_4OH till alkaline; then $(NH_4)_2CO_3$ will precipitate $SrCO_3$ and $CaCO_3$. Filter and dissolve off the paper with acetic acid as before.
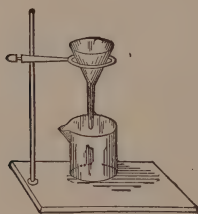
$CaCO_3$ and $SrCO_3$, which when treated with acetic acid, will give a solution of the acetates of Ca and Sr.

Reserve about one-fourth of this acetate solution. To the remainder add dilute K_2SO_4 solution, which will precipitate $SrSO_4$. (If only slight amounts of Sr are present, it may take some time to complete the precipitation. If a large amount

---

* The object of removing the $K_2Cr_2O_7$ is to furnish a colorless solution wherein the Sr or Ca precipitates may be more clearly discerned. It is not absolutely necessary and, in case the amount of Sr and Ca is probably slight, might be omitted, as the operation is always attended with some loss.

of Ca is present, some $CaSO_4$ may also be thrown down.) Filter.
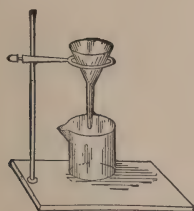
SrSO$_4$.

Ca(C$_2$H$_3$O$_2$)$_2$ or CaSO$_4$.

Test filtrate for Ca by adding ammonium oxalate, which will precipitate calcium oxalate, white.

If there is any question about the precipitate thrown out by K_2SO_4 being Sr, make confirmatory test on reserved portion, either by flame test (page 71), or by adding $CaSO_4$, and allowing to stand twelve hours. $CaSO_4$ will precipitate Sr as $SrSO_4$, but of course cannot precipitate Ca.

QUESTIONS ON GROUP V.

Why add NH_4Cl before precipitating the group with $(NH_4)_2CO_3$?

Why dissolve the precipitated carbonates in acetic acid rather than HCl?

Why use the acid chromate of potassium ($K_2Cr_2O_7$) in testing for Ba rather than the neutral chromate (K_2CrO_4)?

Why precipitate Sr and Ca after separation of Ba with $K_2Cr_2O_7$?

OUTLINE SCHEME FOR ANALYSIS OF GROUP V
To clear filtrate from Group IV add $(NH_4)_2CO_3$.

Precipitate=Ba, Sr, and Ca. Add K₂Cr₂O₇, if necessary to precipitate Ba.		Solution=Mg. Test for Mg with Na₂HPO₄ (page 75).
Precipitate=BaCrO₄.	Solution = Sr and Ca. Reprecipitate Sr or Ca with (NH₄)₂CO₃. Dissolve in HA. Remove Sr with K₂SO₄ and alcohol, and test filtrate for Ca with (NH₄)₂C₂O₄ (page 73).	

CHAPTER VIII.

METALS OF GROUP VI.

THE ALKALINE METALS, K, Na, NH, Li.

POTASSIUM, sodium, and the hypothetical "metal" ammonium are the bases of a very large number of salts used in the arts and sciences.

As a class the metals may be distinguished from the alkaline earths by the ready solubility of their hydrates and carbonates. The hydrates of the alkaline earths are only sparingly soluble, and their carbonates are insoluble.

The salts of lithium are also soluble, but are used in relatively small amounts.

These bases are not precipitated by any group reagent and must be detected by individual tests.

POTASSIUM, K (Kalium).

The Metal. — Atomic weight 39.1. Occurs as carbonate in wood ashes, as nitrate in the "niter beds" of India, etc., as chloride from the Stassfurt deposit in the Province of Saxony, Prussia, as the mineral sylvite, also in the double chloride of magnesium and potassium (carnallite).

Properties. — Melting-point 62.5°. Potassium is a silver white metal. It decomposes water at ordinary temperatures evolving enough heat to ignite the liberated hydrogen.

Compounds. — The salts of potassium are generally soluble in water. Among the more important compounds is the hydroxide KOH. This is used very largely as a starting point in the preparation of many of the medicinal salts of potassium. It

78

may be made by treating potassium carbonate with slaked lime, according to the following reaction:

$$CaO_2H_2 + K_2CO_3 = CaCO_3 + 2 KOH.$$

The carbonate obtained from wood ashes is known as "salts of tartar," and in the impure form as pearl ash. Potassium carbonate is also made in large quantities from the native chloride found in the Stassfurt deposit.

The bicarbonate $KHCO_3$, or saleratus, may be obtained by saturating the carbonate with CO_2.

$$K_2CO_3 + CO_2 + H_2O = 2 KHCO_3.$$

This salt, used in cooking, proves more or less irritating, and has been practically replaced by the corresponding sodium salt, $NaHCO_3$ or "cooking soda."

Potassium nitrate, KNO_3, also called niter and saltpeter, is used in medicine as a diuretic. It gives off oxygen easily, and is consequently a good oxidizing agent, and as such is a constituent of fireworks, gunpowder, etc.

KNO_3 may be prepared from the cheaper sodium nitrate by double decomposition with potassium chloride.

$$NaNO_3 + KCl = KNO_3 + NaCl.$$
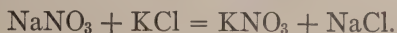
Potassium bromide, used as a sedative, may be prepared by treating caustic potash, KOH, with bromine.

$$6 Br + 6 KOH = 5 KBr + 3 H_2O + KBrO_3.$$

The bromate, $KBrO_3$, is separated by crystallization.

Potassium iodide may be made in a similar manner by substituting iodine for the bromine. Potassium iodide is very soluble, being dissolved in less than its own weight of water. In the laboratory potassium iodide is used as a solvent for iodine, and as a reagent.

Potassium cyanide, KCN, an extremely poisonous compound, is used by jewelers for cleaning silver, etc., and in the arts for the preparation of double salts used in electro-plating. It is

decomposed by CO_2, forming K_2CO_3 and liberating hydrocyanic acid.

Potassium ferrocyanide and ferricyanide are considered under cyanogen compounds in Chapter XXV.

Potassium chlorate may be prepared by treating a hot solution of the hydroxide with chlorine gas. The reaction is the same as that given for the preparation of the bromide, and results in five molecules of the potassium chloride to one of the chlorate.

Potassium sulphide, K_2S, is soluble in water and, in common with other alkaline sulphides, is a solvent for sulphur, thereby forming a number of polysulphides.

The pentasulphide, K_2S_5, is known as "liver of sulphur" or sulphuret of potassium.

Potassium platinic chloride, K_2PtCl_6, and potassium acid tartrate, $KHC_4H_4O_6$, are only sparingly soluble and may be precipitated by addition to the solution of an equal volume of alcohol, in which they are quite insoluble.

The potassium acid tartrate, or bitartrate, is also called cream of tartar, and is used in the manufacture of baking powder. This salt separates from wine vats, it being precipitated by the alcohol produced during the process of fermentation of the grape juice. In this impure form it is known as argols, or crude tartar.

Analytical Reactions. — The presence of potassium salts may be detected spectroscopically or by the violet color given to the flame observed through blue glass. Make comparative tests with known solutions of sodium and potassium salts, using blue glass of sufficient thickness to obscure the yellow (Na) ray.

Note. — In making the flame test the best results are obtained by evaporating a little of the *original* solution to dryness, moistening with HCl and then taking up on a loop of clean platinum wire.

The platinic chloride test may be made as follows:

Add a few drops of HCl to a little of the solution, then evaporate to dryness. Keep at a low red heat till all ammonium salts have been driven off, cool, and take up in a little (not

more than 5 c.c.) distilled water. Add a few drops of H_2PtCl_6 and about 5 c.c. of alcohol. Set aside for some time. K_2PtCl_6, yellow, will crystallize out recognizable under the microscope (Plate III, Fig. 3).

Sodium, Na (Natrium).

The Metal. — Atomic weight 23.0. It occurs principally as chloride in sea-water and in mineral deposits, and to a lesser extent as nitrate, Chili saltpeter, and as cryolite, the double fluoride of aluminium and sodium, (Na_3AlF_6), found in Greenland.

Properties. — Melting-point 95.6°. Sodium is a shiny metal of cheese-like consistency, easily cut with a knife. It tarnishes quickly in the air, with the formation of the hydroxide. Sodium, and potassium also, can be distilled in atmospheres which do not affect the metal.

Compounds. — Sodium peroxide, or dioxide, Na_2O_2, may be prepared by simply heating metallic sodium in dry air. It is a yellowish white powder used somewhat in dental practice for the preparation of alkaline solutions of H_2O_2:

$$Na_2O_2 + 2\,H_2O = 2\,NaOH + H_2O_2.$$

The alkaline peroxide is much more efficient as a bleaching agent than the neutral or acid preparations.

Sodium hydroxide, NaOH, is found in trade in several forms. The stick " caustic soda, " used in chemical laboratories, contains anywhere from five to thirty per cent. of water. In a powder form, less pure than the above, it is known as " concentrated lye," Babbitt's potash, etc., and is used for cleaning, and in the manufacture of soap. Sodium hydroxide is caustic or escharotic in its action upon animal tissue. It may be made experimentally by experiment No. 49, page 376.

Sodium carbonate, Na_2CO_3, crystallizes with ten molecules of water. In this form it is known as " sal soda," or washing soda. It is used as a starting point in the manufacture of other

sodium salts. Sodium carbonate is produced from sodium chloride by the Le Blanc process, in which the following reactions are involved:

$$(1) \ 2 \ NaCl + H_2SO_4 = Na_2SO_4 + 2 \ HCl.$$
$$(2) \quad Na_2SO_4 + 2 \ C = Na_2S + 2 \ CO_2.$$
$$(3) \quad Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$
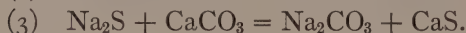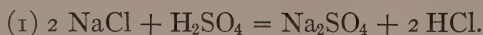
The last two reactions are combined in the actual process of manufacture, and the mixture of sodium sulphate, carbon, and calcium carbonate are heated together with the resulting formation of " black ash " from which is produced pure sodium carbonate.

More recent processes are the Solvay or ammonia process, depending on the following reaction:

$$NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl,$$

and the cryolite process in which the source of the sodium is the double fluoride of sodium and aluminum, Na_3AlF_6. By this process the cryolite is heated with lime, forming calcium fluoride and sodium aluminate.

$$Na_3AlF_6 + 3 \ CaO = 3 \ CaF_2 + Na_3AlO_3.$$

Note. — According to Remsen the sodium aluminate probably consists of a variety similar in composition to the potassium aluminate given on page 57 ($NaAlO_2$ and Na_2O until water is added).

Sodium bicarbonate, $NaHCO_3$, also called cooking soda, is largely used like " saleratus " ($KHCO_3$) as a source of carbon dioxide in the leavening or aerating of bread.

Sodium bicarbonate is hydrolyzed by water, i.e., it dissociates in solution forming sodium hydroxide and carbonic acid. The carbonic acid is a weak acid furnishing very few hydrogen ions, while the hydroxide is a strong base. It follows that the reaction of such a solution is alkaline to litmus, although the salt answers to our definition of an acid salt. This is true of sodium car-

bonate (the products of hydrolysis being NaOH and $NaHCO_3$), and in a similar manner of corresponding potassium salts.

Sodium chloride NaCl, common salt, exists in sea-water to the extent of 2.7%, and is, to some extent, obtained from this source, although the greater amount is produced by the salt mines. Salt is a constituent of all of the body fluids, and can be easily obtained as cubical crystals by the evaporation of urine or of dialyzed saliva.

Physiological, or normal salt solution, contains about 0.7% of sodium chloride, and has practically the same osmotic pressure as blood.

The term "physiological" is to be preferred to the term "normal," as normal salt solution is also properly applied to a solution used in volumetric analysis containing exactly 5.85% of sodium chloride (see page 159).

Sodium nitrate, $NaNO_3$, Chili saltpeter, is valuable as a fertilizer, but too hygroscopic to be used in the same way as potassium nitrate, in the preparation of gunpowder, fireworks, etc.

Sodium phosphate, trisodic phosphate, Na_3PO_4, is a crystalline salt, soluble in water, but of slight interest in Dental Chemistry. It is easily decomposed by CO_2, forming Na_2HPO_4 and Na_2CO_3.

$$2\,Na_3PO_4 + H_2O + CO_2 = 2\,Na_2HPO_4 + Na_2CO_3.$$
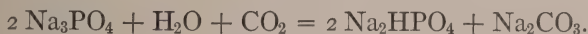
The disodic phosphate, Na_2HPO_4, also called neutral or orthosodium phosphate, is the sodium phosphate of the Pharmacopœia. It is faintly alkaline in reaction, and exists in the body fluids generally. The alkaline reaction (to litmus) of saliva is, in part, due to its presence.

The acid, or monobasic sodium phosphate, NaH_2PO_4, is a translucent crystalline salt found to some extent in the body fluids, particularly the urine, to the acidity of which it is probably a contributing factor, although to a much less extent than was formally supposed.

Sodium potassium tartrate, $KNaC_4H_4O_6$, Rochelle salt, is used in medicine as a mild laxative. It is the product of the double decomposition incident to raising bread with "cream of tartar and soda."

$$KHC_4H_4O_6 + NaHCO_3 = KNaC_4H_4O_6 + CO_2 + H_2O.$$

Sodium sulphate crystallized with ten molecules of water ($Na_2SO_4.10\ H_2O$) is known as Glauber's salt.

Analytical Reactions. — Na may be detected by the use of the spectroscope or by the *persistence* of the yellow flame obtained with a *clean* platinum wire and a colorless Bunsen flame. Make a comparative test with small amount of known sodium salt.
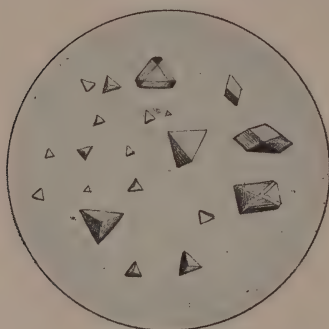
Fig. 6. Uranyl Sodium Acetate.

Sodium salts are soluble with only a very few exceptions. The pyroantimonate, $Na_2H_2Sb_2O_7$, may be precipitated in the cold by a freshly prepared solution of *potassium* pyroantimonate. (Prescott and Johnson, page 228.)

From a solution stronger than 3% and nearly neutral the double acetate of uranyl and sodium ($NaC_2H_3O_2, UO_2(C_2H_3O_2)_2$) may be precipitated. (Fig. 6.) As triple crystalline acetates may also be formed with Mg, Cu, Fe, Ni, and Co, it is recommended to first precipitate the bases of the first five groups and drive off ammonium salts, as in the test for K with H_2PtCl_6.*

LITHIUM, Li.

Atomic weight 6.94. The carbonate, citrate, bromide, and chloride are used in medicine.

The value of lithium salts as uric acid solvents is questionable, because of the insolubility of the phosphate (page 242).

* Behrens's Manual of Microchemical Analysis, page 32.

The presence of lithium is easily shown after the precipitation of strontium by the intense carmine color given to the Bunsen flame.

The spectroscope furnishes a very delicate and positive test for this element.

AMMONIUM, NH_4.

Ammonia is obtained in large part from the ammoniacal liquor of the gas works, where illuminating gas is made by the distillation of coal. The liquor, charged with ammonia, is treated with hydrochloric or sulphuric acid, thus producing an impure salt which is subsequently purified or used as a source of NH_3 in the preparation of pure ammonium compounds.

$$(NH_4)_2SO_4 + CaO_2H_2 = CaSO_4 + 2\,NH_3 + 2\,H_2O.$$
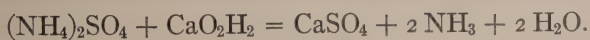
Compounds. — Ammonium hydroxide, NH_4OH, has never been separated as such, free from water. It undoubtedly exists, however, in aqueous solutions of ammonia gas.

$$NH_3 + H_2O = NH_4OH.$$

The negative hydroxyl ions of this ammonium base are not separated by dissociation to the same degree as those of potassium hydroxide in solution; hence, it is a weaker base.

Aqua ammonia of the pharmacopeia contains 10% NH_3. The "stronger water of ammonia" contains 28% of the gas, which is about as strong a solution as it is safe to make for shipment, and containers should never be more than four-fifths full. The 28% solution is referred to as 26° ammonia, the degree indicating the specific gravity as taken by the Baumé hydrometer.

Ammonium carbonate exists in solution. The salt used in medicine under this name is really a mixture of ammonium bicarbonate, NH_4HCO_3, and the carbamate, $NH_4NH_2CO_2$.

This salt gives off NH_3 gas, and moistened with ammonia water and perfumed constitutes "smelling salts."

Ammonium chloride, sal ammoniac (NH_4Cl), white, crystalline, is made by neutralizing NH_4OH with hydrochloric acid. Ammonium chloride will sublime unchanged. It is freely soluble in water, its solution acts as an electrolyte and will dissolve metals from an alloy. If a silver spoon or a ten cent piece is allowed to remain for ten or twelve hours in a dilute solution of ammonium chloride, an appreciable amount of copper will pass into solution, coloring it blue or green, according to the concentration of the copper solution. It also dissolves some metallic oxides, as zinc oxide.

As saliva is known to contain considerable NH_4Cl, the above facts should be studied carefully in considering the action of saliva on substances used for filling teeth, although the solvent action of NH_4Cl in saliva is nothing like what it is in water.

Ammonium nitrate, NH_4NO_3, crystallizes in large six-sided prisms without water of crystallization. It is very soluble in water. It melts at 165° C. Heated to 210° C., it decomposes into nitrous oxide and water. Above 250° C., other oxides of nitrogen are produced, so in the preparation of nitrous oxide for dental anesthesia, care should be taken to keep the temperature of the reaction between these limits.

Ammonium acetate, $NH_4C_2H_3O_2$. A solution of this salt, containing about 7%, is used in medicine as a diaphoretic. The solution is also known as Spirit of Mindererus. In analytical chemistry, it is used as a solvent for lead sulphate.

Ammonium sulphate, $(NH_4)_2SO_4$, is a white crystalline salt soluble in water, not used medicinally, but largely used as a reagent in physiological chemistry. It melts at 140° C., and at a higher temperature it decomposes.

Ammonium sulphide, $(NH_4)_2S$, is used as a solvent and reagent. It may be prepared by saturating ammonia water, NH_4OH, with H_2S, then adding an equal volume of ammonia water:

$$NH_4OH + H_2S = NH_4SH + H_2O,$$

and $$NH_4SH + NH_4OH = (NH_4)_2S + H_2O.$$
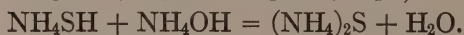
A polysulphide, made by dissolving sulphur in $(NH_4)_2S$ is the reagent used in dissolving the sulphides of Group II (*b*) and in precipitating the zinc group.

Ammonium phosphates. Ammonium, like other univalent bases, is capable of forming, with phosphoric acid, three different salts. $(NH_4)_3PO_4$ is very unstable. The diammonium phosphate has been used, to a slight extent, in medicine (Br. P.) and has been shown to be an energetic activator of lactic acid organisms.*

The importance of this fact, in relation to dental caries, has yet to be demonstrated.

Microcosmic salt is a name given to a double ammonium sodium phosphate $(NH_4NaHPO_4.4H_2O)$ used in blowpipe analysis.

Analytical Reactions. — Ammonium salts are generally soluble. H_2PtCl_6 precipitates the double chloride $(NH_4)_2PtCl_6$, similar in appearance and crystalline form to the corresponding potassium salt (Plate III, Figs. 1–3).

Ammonium salts are most easily detected by the evolution of ammonia gas (NH_3) whenever they are heated with fixed alkali, NaOH or KOH.

The test may be made upon the original solution by boiling in a test-tube with a little 10% NaOH, and the escaping NH_3 may be detected by the odor or, better, by suspending in the upper part of the tube a piece of *moistened red* litmus paper, which is promptly turned blue by the " volatile alkali." The litmus-paper test is more delicate than the odor test. Care should be taken that the paper does not touch the sides of the tube, as it may come in contact with traces of NaOH.

Many ammonium solutions give off NH_3 gas without the aid of any fixed alkali. Common examples are the carbonate, acid carbonate, hydrate, sulphide, and sulph-hydrate.

* Dr. Percy Howe in Dental Cosmos, Jan., 1912.

QUESTIONS ON GROUP VI.

Why use alcohol in the precipitation of ammonium or potassium as double chloride with platinum?

Why are the flame tests preferably made with chlorides of the metals?

Why is ammonia called the volatile alkali, and what are the fixed alkalis from which it is thus distinguished?

Analysis of Groups III, IV, and V.

(When phosphates, borates, or oxalates are present.)

To the filtrate from Group II add NH_4Cl and NH_4OH in slight excess. Heat to boiling and add $(NH_4)_2S$ slowly (always keeping the solution at the boiling-point) until precipitation is complete. Filter as rapidly as possible and wash with hot water, adding occasionally a little $(NH_4)_2S$.

The filtrate, which may contain the barium and potassium groups, must be concentrated by evaporation, filtered if necessary, and set aside.* The precipitate may contain MnS, ZnS, CoS, NiS, FeS, $Al(OH)_3$, and $Cr(OH)_3$ with phosphates or oxalates soluble in acids only. The color of the precipitate will give some indication of what is present. Test the precipitate for Mn by fusing a part with KNO_3 and Na_2CO_3.

Treat the precipitate with *cold dilute* HCl in which CoS and NiS alone are insoluble. Filter. Treat insoluble residue for Co and Ni according to directions on page 67.

The HCl solution, which may contain Mn, Zn, Fe, Cr, and Al as chlorides, and phosphates and oxalates soluble in acids, and which is green or violet if much Cr is present, is boiled with a few drops of HNO_3 until all the H_2S is expelled.

Test a *small* portion of the solution for Fe exactly as in

---

* If Ni is present, the filtrate is frequently brown or black, since NiS is somewhat soluble in an excess of $(NH_4)_2S$, especially if much NH_4OH is present. The NiS may be precipitated, after evaporation, by acidifying with HCl.

analysis of Group III given on page 59. Of the remainder of the solution take about one-third, and add dilute H_2SO_4.

A white precipitate may contain $BaSO_4$, $SrSO_4$, and possibly $CaSO_4$. Filter, wash precipitate, and fuse with a mixture of Na_2CO_3 and K_2CO_3.

Note. — The mixture of the two carbonates in molecular proportions fuses at a lower temperature than either salt alone.

Filter and wash the carbonates thus formed, dissolve them in acetic acid and examine this solution for Ba, Sr, and Ca as directed under the Ba group. To the filtrate from the precipitate produced by H_2SO_4, or to the solution in which H_2SO_4 has failed to give a precipitate, add three times its volume of alcohol; Ca, if present, is precipitated as white $CaSO_4$, and its presence may be confirmed by dissolving the precipitate in water and adding $(NH_4)_2C_2O_4$, which precipitates CaC_2O_4, white.

To the rest of the HCl solution add ferric chloride, carefully, till a drop of the solution gives, when mixed with a drop of ammonic hydrate, a yellowish precipitate. To the solution add Na_2CO_3 or K_2CO_3 till the acid is nearly neutralized, then add excess of freshly precipitated $BaCO_3$, and allow to stand over night. Filter.
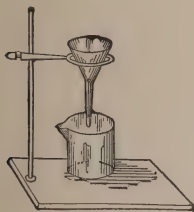
Cr and Al as hydrates. (Fe as phosphate or hydrate and $BaCO_3$.)

$MnCl_2$, $ZnCl_2$, and possibly members of Group V.

Transfer the precipitate to a small beaker and boil for some time with NaOH or KOH. The Al will be converted into the aluminate $KAlO_2$. The phosphate will be more or less completely changed to potassium or sodium phosphate. Filter.
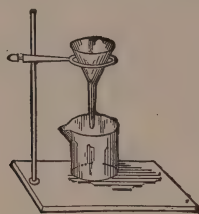
Cr(OH)$_3$, BaCO, etc.

KAlO$_2$ and Na$_2$HPO$_4$.

Test precipitate for Cr as on page 58. Add HNO$_3$ to filtrate till acid, then divide into two parts; test one for P$_2$O$_5$ with (NH$_4$)$_2$MoO$_4$.

Test the other for Al by adding NH$_4$OH till alkaline, when precipitate will be AlPO$_4$, insoluble in acetic acid.

To the solution of Mn and Zn chlorides add a little HCl and boil. Then make alkaline with NH$_4$OH, add (NH$_4$)$_2$S, warm slightly and filter. The precipitate (MnS and ZnS) may be dissolved in cold dilute HCl and tested for Mn and Zn as in analysis of Group IV, page 67.

OUTLINE SCHEME FOR ANALYSIS OF GROUPS III, IV, AND V.

(Phosphates, oxalates, borates, etc., being present.)

To filtrate from Group II add NH$_4$Cl and NH$_4$OH. Heat and add (NH$_4$)$_2$S. Filter rapidly.

Precipitate=MnS, ZnS, CoS, NiS, FeS, Al(OH)$_3$, Cr(OH)$_3$, also phosphates, etc., soluble in acids only. Fuse part of precipitate and test for Mn (page 63). Treat remainder c̄ cold dilute HCl.					*Filtrate*, members of Ba and K groups
Residue= CoS and NiS. Make borax-bead test and separate Co if necessary, c̄ KNO$_2$ (page 67).	*Solution*=Mn, Zn, Cr, and Al. Divide solution into three parts of about 1/8, 2/8, and 5/8, respectively, and treat as follows:				
	I. Test small portion for Fe (page 55).	II. To second portion add dilute H$_2$SO$_4$.		III. To third portion add FeCl$_3$ to combine c̄ H$_3$PO$_4$, etc., then add Na$_2$CO$_3$ or K$_2$CO$_3$, and BaCO$_3$ (page 89).	
		Precipitate may be BaSO$_4$, SrSO$_4$ or CaSO$_4$. Filter, wash, fuse c̄ Na$_2$CO$_3$ and K$_2$CO$_3$. Dissolve fusion in H̄A and analyze for Group V.	*Solution=* CaSO$_4$. Add alcohol; if precipitate occurs, filter, dissolve in H$_2$O, and test with ammonium oxalate.	*Precipitate=* Cr, Al, Fe, and BaCO$_3$. Boil precipitate c̄ NaOH and filter.	*Solution=* Mn and Zn. Reprecipitate Mn and Zn as sulphides, and test according to page 67.
				Residue= Cr, BaCO$_3$, etc. Test for Cr as on page 59.	*Solution=* KAlO$_2$. Test for Al as on page 59.

CHAPTER IX.

ANALYTICAL REACTIONS OF THE ACIDS.

In the analytical processes thus far described we have considered only the separation and detection of the basic or metallic part of the salt (positive ions), that is, we have analyzed a solution of ferric chloride, and found the iron only. It is necessary to find the chlorine (negative ion). Before making any examination for negative ions, it will be possible to save a considerable amount of both time and labor by first carefully considering what acids are capable of forming soluble salts with the bases which have already been detected. To facilitate this consideration a table of solubilities will be found below and on the following page, by a careful study of which it will be possible to select such acids as are most likely to be present in the unknown solution under investigation, and also to neglect a number of acids which, from the solubility of their salts, together with the character of the solution (acid, alkaline, neutral and aqueous, or otherwise), will necessarily be absent.

TABLE SHOWING THE SOLUBILITY OF SALTS

	K	Na	NH$_4$	Mg	Ba	Sr	Ca	Mn	Zn	Co	Ni	Fe	Fe$_2$
Acetate	w	w	w	w	w	w	w	w	w	w	w	w	w
Arsenate	w	w	w	a	a	a	a	a	a	a	a	a	a
Arsenite	w	w	w	a	wa	wa	a	a	a	a	a	a	a
Borate	w	w	w	wa	a	a	a	a	a	a	a	a	a
Bromide	w	w	w	w	w	w	w	w	w	w	w	w	w
Carbonate	w	w	w	a	a	a	a	a	a	a	a	a	a
Chlorate	w	w	w	w	w	w	w	w	w	w	w	w	w
Chloride	w	w	w	w	w	w	w	w	w	w	w	w	w
Chromate	w	w	w	w	a	wa	wa	w	w	a	a	ai	w
Cyanide	w	w	w	w	wa	w	w	a	a	ai	ai	ai	
Iodide	w	w	w	w	w	w	w	w	w	w	w	w	w
Nitrate	w	w	w	w	w	w	w	w	w	w	w	w	w
Oxalate	w	w	w	a	a	a	a	a	a	a	a	a	a
Oxide	w	w		a	w	w	a	a	a	a	a	a	a
Phosphate	w	w	w	a	a	a	a	a	a	a	a	a	a
Silicate	w	w		a	a	a	a	a	a	a	a	a	a
Sulphate	w	w	w	w	i	i	wi	w	w	w	w	w	w
Sulphide	w	w	w	wa	w	w	w	a	a	a	a	a	a
Sulphocyanate	w	w	w	w	w	w	w	w	w	w	w	w	w
Tartrate	w	w	w	wa	a	a	a	wa	a	w	a	wa	w

TABLE SHOWING THE SOLUBILITY OF SALTS. — *CONCLUDED.*

	Cr₂	Al₂	Sb	Sn''	Sn^IV	Au	Ag	Hg₂	Hg	Pb	Bi	Cu	Cd
Acetate..............	w	w	w	w	w		wa	wa	w	w	w	w	w
Arsenate............	a	a	a	a	a		a	a	a	a	a	a	a
Arsenite............			a	a	a		a	a	a	a		a	wa
Borate.............	a	a		a			a			a	a	a	wa
Bromide............	w	w	wa	w	w	w	i	ai	wa	wi	wa	w	w
Carbonate..........							a	a	a	a	a	a	w
Chlorate...........	w	w		w			w	w	w	w	w	w	w
Chloride...........	w & i	w	wa	w	w	w	i	ai	w	wi	wa	w	w
Chromate..........	a		a	a			a	a	wa	ai	a	w	a
Cyanide...........	a					w	i		w	a	wa	a	a
Iodide.............	w	w	wa	w	w	a	i	a	a	wa	a	a	w
Nitrate............	w	w		a	a		w	w	w	w	a	w	w
Oxalate............	w	a	a	a	w		a	a	a	a	a	a	a
Oxide..............	a & i	a & i	a	a	a & i		a	a	a	a	a	a	a
Phosphate..........	a	a	a	a	a		a	a	a	a	a	a	a
Silicate............	a	ai								a		a	
Sulphate...........	w &a	w	a	w	w		wa	wa	wa	a	a	w	w
Sulphide...........			a	a	a	a	a	a	a	a		a	wa
Sulphocyanate......	w				w		i		w	a		a	wa
Tartrate...........	w	w	w	wa			a	a	a	a	a	wa	wa

w, soluble in water; a, insoluble in water, soluble in acids; i, insoluble in water or acids; wa, sparingly soluble in water, readily soluble in acids; wi, sparingly soluble in water and acids; ai, sparingly soluble in acids only.

In this connection it is well to remember that practically all nitrates and chlorates are soluble in water; sulphates are mostly soluble, except those of barium, strontium, and calcium. Phosphates (di- or trimetallic), silicates, oxalates, and borates are practically insoluble, except those of the alkaline metals. This latter statement is also true of carbonates, except that some of the carbonates will dissolve to an appreciable extent in water containing carbon dioxide. Chlorides, bromides, and iodides are nearly all soluble except those of the first-group metals. Sulphides are insoluble except those of Groups V and VI. Acid salts are usually more soluble than neutral salts.

In making qualitative tests for the negative ions it is not necessary to separate them one from the other, as it is in the case of metals; hence the tests are individual ones, usually made upon the original substance or solution, and often require confirmation before conclusive evidence is obtained. The grouping is, therefore, simply for convenience, as it thus becomes possible to exclude a considerable number of acids by a single general test.

Acid Groups (negative ions).

Group I may include such acids as give effervescence when their dry salts are treated with *dilute* H_2SO_4, as H_2CO_3, H_2S, $H_2S_2O_3$, H_2SO_3 and HCN.

Group II may include acids giving a precipitate with $AgNO_3$ in dilute HNO_3 solution, as HCl, HBr, HI, HCN, HCNS, HNO_2, HClO, H_4FeCy_6, H_3FeCy_6, $H_2S_2O_3$, H_2S and HPH_2O_2.

This second group may be further subdivided into three parts according to the color of the precipitate obtained (pages 95 and 97).

Group III may include acids forming insoluble salts with $BaCl_2$ or $CaCl_2$ and not found in Groups I or II, as H_2SO_4, $H_2C_2O_4$, H_3PO_4, H_3BO_3, H_2CrO_4 and H_2SiO_3.

Group IV: We may put in Group IV any acids not included in the foregoing groups. Of common occurrence are nitric (nitrates), chloric (chlorates), and acetic (acetates).

Detection of Acids of Group I.

(Acids effervescing with dilute sulphuric acid. H_2CO_3, H_2S, H_2SO_3, $H_2S_2O_3$, HCN.)

To a test-tube a quarter full of the unknown solution, or a little dry substance on a watch-glass, add dilute H_2SO_4. If solution is very dilute, concentrate it before making test, as a slight amount of gas might be absorbed by the water. Watch carefully for any escape of gas and note any odor which may be given off.

Carbonates evolve CO_2, odorless, but if passed into lime-water or baryta-water will give white precipitate of $CaCO_3$ or $BaCO_3$.

Sulphides evolve H_2S, odor of rotten eggs. Confirm by adding a little dilute H_2SO_4 to the suspected powder (or solution) in a test-tube and holding over the mouth of the tube a piece of filter-paper wet with a solution of lead acetate. The test-tube may be warmed slightly to expel the gas, when a dark-

colored stain will appear on the filter-paper, due to the formation of PbS.

Sulphites evolve SO_2, odor of burning sulphur. Sulphites in *neutral* solution may be further identified by the deep-red color produced with ferric chloride. The color is discharged upon addition of dilute acids, HCl, or H_2SO_4 (difference from HCNS).

Thiosulphates *also* evolve SO_2, but at the same time the mixture becomes cloudy from precipitation of sulphur.*

Thiosulphates in neutral solution treated with ferric chloride give a violet to purple color, fading (rapidly upon warming) to a colorless solution. In mixtures of sulphites and thiosulphates both acids may often be detected by the use of $FeCl_3$, the deep-red coloration of the mixed acids rapidly fading to the lighter red of $Fe_2(SO_3)_3$ (not to colorless solution).

Cyanides evolve HCN, odor of peach-stones. (Mercuric cyanide does not respond to this reaction.) Confirm by reactions given under Group II.

Preliminary Tests for Common Acids of Groups ii and iii.
(In preparatory courses the acids given in this list may be sufficient.)

From the acids of Group II and III it may be desirable to select for laboratory practice, at least at the beginning of the acid work, the more common members of the groups. These will be HCl, HBr, HI, HCN, and H_2S of Group II and H_2SO_4, $H_2C_2O_4$, and H_3PO_4 of Group III; and tests for them may be made as follows:

Chlorides give with $AgNO_3$ in presence of HNO_3 a white curdy precipitate of AgCl, much more freely soluble in ammonia than any other acid of the group here given except the cyanide

---

* Sulphides may also precipitate sulphur in presence of compounds capable of oxidizing the H_2S, such as $FeCl_3$. In the absence of sulphates either H_2SO_3 or $H_2S_2O_3$ can be oxidized to H_2SO_4 by heating with HNO_3 and a precipitate of $BaSO_4$ obtained with $BaCl_2$.

AgCN, but HCN is a member of the *first* acid group and would have been previously detected.

Bromides with $AgNO_3$ and HNO_3 give a precipitate of AgBr similar in appearance to AgCl, but with a slightly yellowish color and only sparingly soluble in NH_4OH.

The tests, described on page 97, should also be made if bromides or iodides are suspected in the solution.

Cyanides, see Group I.

Sulphides will give a black precipitate with $AgNO_3$, and have been previously considered in Group I.

Sulphates may be detected by first acidifying the solution strongly with HCl (filtering out a precipitate if any occurs) and adding a solution of $BaCl_2$; a white precipitate will then be $BaSO_4$, showing presence of sulphates in solution tested.

Phosphates in a solution containing HNO_3 and free or nearly free from HCl will give, with ammonium molybdate, a yellow crystalline precipitate of ammonium phosphomolybdate.

Oxalates may be detected, in a solution free from sulphates and which is slightly acid with acetic acid, by simple addition of calcium chloride, which will precipitate CaC_2O_4, white and crystalline.

DETECTION OF ACIDS OF GROUP II.

(Giving precipitate with $AgNO_3$ in presence of dilute HNO_3.)

To the solution to be tested add a *very* slight amount of HNO_3 and a few cubic centimeters of $AgNO_3$ solution. A precipitate indicates acids of this group.

(*a*) If the precipitate is white, the presence of chlorides (HCl), cyanides (HCN), sulphocyanates (HCNS), ferrocyanates (H_4FeCy_6), hypochlorites (HClO),* or nitrites (HNO_2) is indicated.

---

* Precipitate is AgCl. Reaction is $3\ NaClO + 3\ AgNO_3 = 2\ AgCl + AgClO_4 + 3\ NaNO_3$.

To separate or identify these silver precipitates allow to settle, decant the supernatant fluid, and add NH_4OH. Shake thoroughly, when the chloride (AgCl), cyanide (AgCN), and nitrite ($AgNO_2$) will dissolve easily, the sulphocyanate (AgCNS) and the ferrocyanide ($Ag_4Fe(CN)_6$) slowly or slightly.

If HCNS, or $H_4Fe(CN)_6$ is indicated, test original solution with a few drops of $FeCl_3$. Sulphocyanates or thiocyanates (HCNS) give a deep blood-red solution. The color is soluble in ether and may be discharged by $HgCl_2$. Ferrocyanides ($H_4Fe(CN)_6$) give a deep-blue precipitate. (See page 55.)

Acids forming white silver precipitates, easily soluble in ammonia, may be distinguished as follows:

Chlorides (HCl) may be distinguished from HBr and HI by the ready solubility of the silver precipitate in NH_4OH. If bromides and iodides are present, liberate the halogens by means of MnO_2 and H_2SO_4 and pass the mixed gases into a solution of aniline in acetic acid (4 c.c. of saturated aqueous solution of aniline and 1 c.c. glacial acetic acid). Iodine gives no precipitate, bromine gives a white one and chlorine a black one. (Prescott and Johnson, page 336.)

This is a delicate and very satisfactory test for bromine but not so delicate for chlorine in the presence of bromides. For such cases the following *chloro-chromic anhydride test* is recommended. Neutralize the solution if necessary, evaporate to dryness, transfer residue to a test-tube of rather small diameter, add a little solid $K_2Cr_2O_7$, then concentrated H_2SO_4. Decant the *fumes* into a wider test-tube containing a few cubic centimeters of NH_4OH.

If the chloro-chromic anhydride is evolved, ammonium chromate will be formed. Test by making acid with acetic acid, then adding acetate of lead. A yellow precipitate of lead chromate indicates chlorine in the original solution.

Hypochlorites liberate I from KI without the addition of acid.

Note. — Hypochlorite solutions are usually quite strongly alkaline, and in such cases a considerable amount of iodide is necessary to obtain the characteristic color in chloroform or with starch.

Nitrites liberate I from KI after the addition of acetic acid. They also give a brown coloration with acetic acid and a crystal of ferrous sulphate. (Nitrates require a stronger acid.)

Note. — This test is much more delicate than either of the others given, and if the solution is very dilute it is well to make it, even if the indigo color is not discharged.

Further mix a little of the solution with a few cubic centimeters of dilute indigo solution and shake. The indigo is decolorized by either hypochlorites (HClO) or by nitrites (HNO_2).

Cyanides may be tested for as under Group I. If this test is not conclusive, they may be converted into sulphocyanides by the addition of a few drops of $(NH_4)_2S$ and evaporation on the water-bath to dryness. It may then be dissolved in a little distilled H_2O, filtered and tested with $FeCl_3$.

(*b*) The precipitate is red-brown or orange, soluble in $NH_4OH = H_3FeCy_6$. *Ferricyanide* indicated.

(*c*) The precipitate is black or turns black upon warming: H_2S turns black immediately. HH_2PO_2 starts to precipitate white, but rapidly turns black, $H_2S_2O_3$ precipitates white and turns black slowly or upon heating.

Sulphides (H_2S) and **thiosulphates** ($H_2S_2O_3$) may also be detected as described under Group I, Acids.

(*d*) If the precipitate, originally obtained, is yellow and insoluble in NH_4OH, *iodides* are indicated; if yellowish white and slowly soluble in NH_4OH, *bromides* are probably present.

Iodides and **bromides** (HI and HBr) may be detected in the same solution by adding chlorine water, very cautiously at first, and shaking with chloroform. The chlorine liberates the iodine, which is dissolved by the chloroform with violet color. Excess of chlorine decolorizes the iodine and liberates the bromine which, in turn, is dissolved by the chloroform with yellow to red color.

Acid Group III.

(Acids forming insoluble barium or calcium salts, not included in the Acid
Group I or II.)

The members of this group may be separated from each
other, although this is not necessary unless several members
are present. H_2SO_4, $H_2C_2O_4$, H_2CrO_4, H_2SiO_3, H_3BO_3, H_3PO_4,
separated as follows: To a little of the unknown solution add
2 or 3 c.c. of HCl; a white or gelatinous precipitate which is not
dissolved by dilution with water and warming is probably silicic
acid. Make a bead test with microcosmic salt; the particles of
SiO_2 remain undisturbed by the hot bead, forming the so-called
silicon " skeleton." Filter out the silicic acid and add $CaCl_2$
or a mixture of $BaCl_2$ and $CaCl_2$; a white precipitate will be
$BaSO_4$* (test for *sulphates*), the Ba and Ca salts of all remain-
ing acids of the group being soluble in HCl.

Filter out the $BaSO_4$, and to the filtrate add NH_4OH, which
will cause a precipitate of barium *oxalate, chromate, borate*, and
phosphate. Filter, wash precipitate two or three times, reject
wash-water, then transfer to test-tube by making a small hole in
point of paper and forcibly washing through with the least pos-
sible amount of water; acidulate strongly with acetic acid, which
will dissolve the phosphates and borates, leaving undissolved
the oxalates (BaC_2O_4, white) and chromates ($BaCrO_4$, yellow).
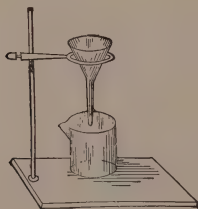
Oxalic and chromic acids as barium salts.

Phosphoric and boric acids.

* If the HCl is too strong, $BaCl_2$ may be precipitated as such, but the pre-
cipitate in this case will form more slowly than the $BaSO_4$; it will have a crystal-
line appearance and will dissolve upon addition of water.

Divide the filtrate into two parts, (*a*) and (*b*). Test one part, (*a*), for H_3PO_4 by adding to it an excess of ammonium molybdate * (in HNO_3), when a yellow precipitate (forming sometimes after several hours' standing) is ammonium phosphomolybdate (test for *phosphates*); the mixture may be warmed to hasten precipitation; the degree of heat should not exceed 40° C., as the ammonium molybdate might be decomposed, giving a yellow precipitate similar to the phosphomolybdate.

Note. — If As is present, it must be removed by H_2S before testing for H_3PO_4.

Test the other part, (*b*), for H_3BO_3 by evaporating to dryness in a porcelain dish; then moisten with strong H_2SO_4, cover with a little alcohol, and ignite. Boric acid will give to the flame (particularly the edge) of the burning alcohol a green color due to formation of ethyl borate. This color is more easily apparent if the dish is placed in a darkened corner.

A test for H_3BO_3 may also be made with turmeric paper, which if dipped into a solution of boric acid, or of a borate mixed with HCl or H_2SO_4 to slight but distinct acid reaction, and dried at 100°, becomes red; the red color becomes bluish black or greenish black when moistened with a solution of an alkali or an alkaline carbonate. If there is a suspicion that H_2CrO_4 and $H_2C_2O_4$ are both present, dissolve the precipitate of barium oxalate and chromate off the paper with dilute HCl; divide the filtrate into two parts and test one for H_2CrO_4 by addition of H_2O_2, which with chromates in presence of HCl produces a deep-blue solution and ultimately $CrCl_3$.

In the *absence* of chromates, the precipitate being white, oxalates may be confirmed by coloring the second part of the solution a faint pink with a dilute solution of $KMnO_4$ and warming, when the color will be discharged.

In the *presence* of chromates, the precipitate being yellow, it will be necessary to test the original solution for oxalates

* Preparation of ammonium molybdate solution, appendix, page 424.

as follows: To a few centimeters of the unknown add alcohol; warm. The chromate will be reduced to $CrCl_3$. Add NH_4OH till alkaline and filter out the precipitate, $Cr(OH)_3$. The filtrate may be tested for oxalic acid as above, or with $CaCl_2$, a white precipitate being CaC_2O_4.

Acids of Group IV.

The remaining acids of importance not included in either of the three preceding groups are nitric, HNO_3, chloric, $HClO_3$, and acetic, $HC_2H_3O_2$.

Nitrates. — Saturate 5 c.c. of a very dilute nitrate solution with $FeSO_4$. Filter and carefully underlay the clear filtrate with concentrated sulphuric acid; a dark ring (pale red-brown to nearly black) at point of contact of the two liquids shows presence of a nitrate.

Chlorates. — A solution free from chlorides or hypochlorites treated with Zn and dilute H_2SO_4 will give a test for HCl if chlorates were originally present, the chlorate having been reduced by the nascent hydrogen:

$$2\,KClO_3 + 6\,Zn + 7\,H_2SO_4 = 6\,ZnSO_4 + K_2SO_4 + 2\,HCl + 6\,H_2O.$$

Boiling with sulphurous acid also reduces $HClO_3$ (and HClO) to HCl.

If the substance is in solid form, a *very small particle* may be warmed with concentrated H_2SO_4. Chlorates detonate and give off yellow fumes of ClO_2:

$$3\,KClO_3 + 2\,H_2SO_4 = 2\,KHSO_4 + KClO_4 + 2\,ClO_2 + H_2O.$$

Acetates give with ferric chloride a red color which is not discharged by $HgCl_2$ (difference from sulphocyanate), but may be discharged by HCl (difference from sulphocyanate and meconate).

A more positive test is the formation of the ethyl ester or acetic ether. A blank test for comparison should always be made, the method of procedure being as follows:

Take two test-tubes of practically equal diameter, mix in each equal volumes of alcohol and strong sulphuric acid; warm the tubes together; then into one introduce a few centimeters of the unknown solution, and into the other an equal volume of water.   Heat again to a boiling-point and compare the odors from the two tubes.   The acetate is easily detected if present.

CHAPTER X.

ANALYSIS IN THE DRY WAY.

In the examination of solid substances much may be learned by a few simple tests directly applied to the substance, which has been reduced (if necessary) to the form of a powder.

Some of these are usually used as preliminary to the solution of the substance and regular analysis in the wet way. These tests may be made quickly, and, with a little elaboration, will often give all the information required regarding an unknown substance.

The practical questions of actual experience are usually simple ones. It is not an analysis of an unknown solution possibly containing all the metals of one or more groups that interests an active practitioner, but a specific inquiry as to whether or not this or that preparation contains or does not contain the necessary or the undesirable ingredient, whether the thing is of the composition or of the strength represented, and a few minutes' work in the laboratory, especially if aided by the microscopical tests given in a subsequent chapter, will frequently be found sufficient to answer questions of this character.

The tests made in the dry way are not as delicate, nor are the results obtained (especially negative ones) as conclusive, as those of a systematic analysis of the substance in solution, and in occasional cases it may be necessary to resort to the more tedious process.

Before undertaking the analysis of a substance, note carefully its physical properties of odor, color, and solubility; also whether it is magnetic, metallic, or crystalline.

The volatile acids, certain ammonium compounds, bromine, and iodine may be detected frequently by their odor.

COLORS OF SALTS AND SOLUTIONS.

The following colored salts are *soluble* in water:

Black......................Silver albuminate (argyrol, etc.).
Violet or purple................Chromic salts and permanganates.
Red.........................$\begin{cases} CrO_3 \text{ and acid chromates, } K_3FeCy_6, \text{ sodium-} \\ \text{nitro-prusside, } H_2PtCl_6. \end{cases}$
Reddish brown or purple-red.....Manganic salts.
Reddish yellow................Ferric salts and $AuCl_3$.
Yellow......................$\begin{cases} \text{Neutral chromates of the alkalis, salts of} \\ \text{uranium.} \end{cases}$
Pale yellow...................K_4FeCy_6 (Potassium ferrocyanide).
Pink..........................Salts of cobalt.
Pale pink.....................Manganous salts.
Green........................$\begin{cases} \text{Ferrous salts, nickel salts, certain copper} \\ \text{salts.} \end{cases}$
Dark green...................Some chromic salts.
Blue-green...................Chromates.
Blue..........................Cupric salts.

The following colored substances are *insoluble* in water:

Black........................$\begin{cases} \text{Carbon and carbides, metals, many metallic} \\ \text{sulphides, oxides of Cu, Fe, Mn, and Pb.} \\ \text{Iodine is bluish black.} \end{cases}$
Red..........................$HgO, HgS, HgI_2, Pb_3O_4, As_2S_2.$
Brick-red....................Amorphous phosphorus, Fe_2O_3.
Light brown..................PbO (litharge).
Yellow.......................$\begin{cases} S, HgO, CdS, As_2S_3, PbI_2, Ag_3PO_4, \text{ ammo-} \\ \text{nium phosphomolybdate, and chromates} \\ \text{of the heavy metals, } PbCrO_4, BaCrO_4. \end{cases}$
Green........................$\begin{cases} \text{Some copper compounds, } Cu_2I_2, \text{ Paris green,} \\ \text{etc., } Cr_2O_3. \end{cases}$
Blue.........................$\begin{cases} \text{Some copper compounds, Prussian blue,} \\ \text{ultramarine; anhydrous salts of cobalt.} \end{cases}$

METHODS OF EXAMINATION.

Powder the substance and apply tests described in this chapter, which will be considered in the following order:

- A. Ignition with free access of air.
- B. Closed-tube test.
- C. Flame test on platinum wire.
- D. Examination with the blow-pipe on plaster slab.
- E. Bead tests on platinum wire.
- F. Special tests, distinguishing or confirmatory.

A. Ignition in Air.

This test may be made on a crucible cover or on platinum foil. If there is any probability of I, Br, Cl, P, or easily reduced metallic compounds in the unknown substance, the platinum foil is likely to be destroyed; hence, the porcelain is recommended.

The heat employed should be very low at first; then it should be gradually increased and the test carefully watched.

The majority of phenomena occurring under A are more easily observed in the test made with closed tube, B, and will be given under that head.

Observed Phenomena.	Indications.
The substance *melts* and steam is given off.	Water of crystallization. NH_4NO_3 or $H_2C_2O_4$, which entirely disappears.
The substance *burns* (a) at comparatively low temperature with blue flame and odor of SO_2 or burning matches.	Sulphur.
(b) With yellow flame and much smoke.	Fat, waxes, resins, etc.
(c) Blackens and then burns at fairly high temperature, leaving white or gray ash.	Carbonaceous matter other than fats, etc.
(d) Blackens without burning.	Formation of oxides of Fe, Co, Ni, or Cu.
Vapors are given off:	
(a) Of a violet color.	Iodine.
(b) Of a red-brown color.	Br or nitrogen oxides.
(c) Of a greenish-yellow color.	Chlorine or ClO_2.
(d) White, practically odorless.	Some ammonium salts, NH_4Cl, $(NH_4)_2SO_4$, etc.

Observed Phenomena.	Indications
(e) White with odor of NH_3.	Ammonium carbonate.
(f) White with odor of garlic.	Arsenic.
(g) White and yellow with ammoniacal or empyreumatic odor.	Organic matter.
The substance decrepitates.	Water held mechanically by crystals, as NaCl, etc.
Examine residue on foil (porcelain); add a drop or two of water and test with litmus-paper.	
If found to be acid.	Acid salts.
If alkaline without blackening.	Fixed alkali hydrates or carbonates.
If alkaline with blackening.	Carbonate formed by combustion of organic compounds.
Add a drop of dilute HCl, effervescence.	Carbonates.

B. Closed-tube Test.

Select a tube of soft glass about five or six inches in length. Seal one end and enlarge slightly. Into the bulb thus formed introduce a few grains of the unknown powdered substance. Heat carefully, making the following tests at various stages of the process. Note the odor of escaping gases.

Test for oxygen by inserting a glowing splinter into the tube.

Test for combustible gases by occasionally applying flame to the open end of the tube.

Bring to the mouth of the tube a clear drop of $Ba(OH)_2$ solution. If the drop becomes turbid, CO_2 is indicated.

Observed Phenomena.	Indications.
STEAM condenses in cold part of tube.	See under A.
OXYGEN is evolved.	A peroxide, chlorate, some oxides (as HgO), alkali nitrates.
CARBON DIOXIDE is evolved.	Carbonates, oxalates (at high temperature), organic matter.
A COMBUSTIBLE GAS is formed:	
(a) Burning with a luminous flame, black residue remains in tube.	Hydrocarbons from organic matter.
(b) Burning with a blue flame.	CO from oxalates.
(c) Burning as in (b) and with odor of SO_2.	H_2S from moist sulphides.
A SUBLIMATE forms in the cooler part of the tube. Examine under microscope.	

OBSERVED PHENOMENA.	INDICATIONS.
Colorless with partial decomposition.	Oxalic acid. Plate I, Fig. 1.
Color is *white* with production of garlic odor, crystalline.	As$_2$O$_3$. Plate I, Fig. 2.
Color is *white* when cold. Yellow when hot, crystalline.	HgCl$_2$. Plate I, Fig. 3.
Color is white — it sublimes directly without melting and blackens with NH$_4$OH.	HgCl.
A white sublimate which by treatment with slaked lime yields NH$_3$.	Ammonium salts. Plate I, Fig. 4.
A white sublimate of As$_2$O$_3$ with black residue in tube and odor of acetic acid.	Paris green.
Sublimate is gray, consisting of small globules which can be made to unite by rubbing.	Hg from HgO, amalgam, etc. Plate I, Fig. 5.
Sublimate consists of reddish yellow to red globules, yellow when cold.	Sulphur.
Sublimate darker than above and reddish yellow when cold.	Native sulphide of arsenic.
Sublimate is brown to black "metallic mirror," soluble in NaClO.	Metallic arsenic.
Ditto; dead black, insoluble in NaClO.	Metallic antimony.
Sublimate is black accompanied by violet vapor.	Iodine. Plate I, Fig. 6.
Sublimate black, turning red when rubbed.	HgS, cinnabar.
No sublimate is formed, but the COLOR CHANGES to	
Yellow when hot, white when cold.	ZnO.
Reddish brown when hot, yellow when cold.	PbO or Bi$_2$O$_3$. (See D.)
Black when hot, red when cold.	HgO (Hg sublimes).
Black when hot, brick-red when cold	Fe$_2$O$_3$.
Dark orange when hot, yellow when cold.	Chromates of Pb, etc.
BLACK RESIDUE without other visible manifestation.	Oxides of Cu, Co, etc. (See A.)
SUBSTANCE MELTS without a sublimate being formed.	Salts of the alkaline metals.

C. Flame Test with Platinum Wire.

Introduce the substance on platinum wire into the edge of the flame. More satisfactory results are sometimes obtained if the solid is first moistened with HCl (page 80, note). The flame is colored as follows: by Na, yellow; K, violet; Ni, carmine; Sr, crimson; Ca, orange-red; Ba, yellowish green; Cu, usually bright green; CuCl$_2$, an intense blue; H$_3$BO$_3$, pale green; Sb, greenish blue; Pb, As, Bi, livid blue.

PLATE I.—SUBLIMATES.
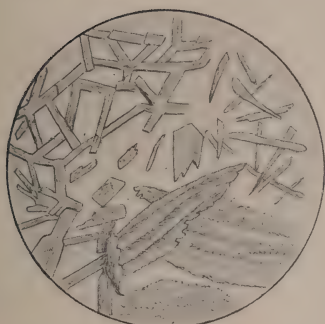
FIG. 1.
Oxalic Acid (Sublimed).
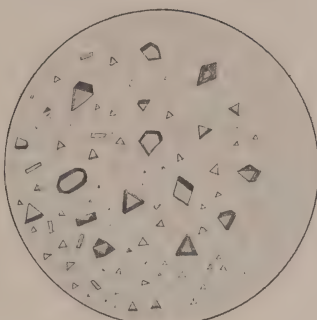
FIG. 2.
Arsenic Trioxide.
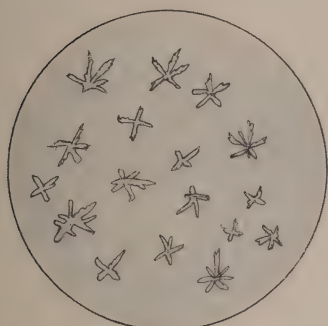
FIG. 3.
Mercuric Chloride (Sublimed).

FIG. 4.
Ammonium Sulphate (Sublimed).
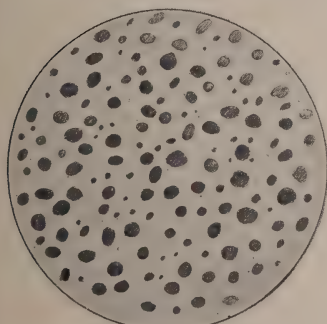
FIG. 5.
Mercury from HgO.
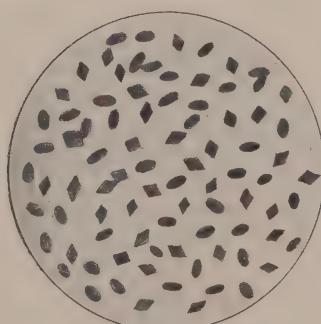
FIG. 6.
Iodine.

D. Blowpipe Test on Plaster.*

Smooth plaster slabs about one inch wide and four inches long are well suited for these tests. These may be prepared by making a magma of calcined plaster and pouring upon a glass plate. Before it hardens mark deeply with a spatula into slabs of desired shape and, after it is thoroughly dried, break as marked.

Make a little depression near one end of the slab and in it place a small amount of the substance to be tested; then if a fine oxidizing flame is made to play over the *surface* of the assay, characteristic coatings of oxide or sublimate may be obtained.

In many cases the character of the substance may be determined more easily by first moistening the assay with various reagents. Tetrachloride of tin, cobalt nitrate, and " sulphur iodide " are the most valuable of the reagents so used. The " sulphur iodide " is not of definite composition, but a mixture of about equal weights of sulphur and potassium iodide.

D. I. *Examination without Reagents.*

Observed Phenomena.	Indications.
Substance melts to bright metallic globules with brownish-yellow deposit near assay. Requires high heat. Assay revolves.	Silver.
Substance melts to bright globule with coating on plaster, deep orange when hot, light yellow when cold.	Lead or bismuth. (See D. II.)
Substance remains or becomes black without melting. No coating on plaster.	Copper or iron. (See A; also F.)
Substance volatilizes with white fumes, but leaves dark stain; gray to black.	Antimony or arsenic. (See F.)
Substance melts with white or gray oxide on assay.	Tin. (See D. III.)
Forms a white or gray oxide *without* fusion. Coating on plaster is yellow over brownish black.	Cadmium.

* Substances sufficiently identified by previous tests have been omitted. This method will be found useful mainly in the identification of metals.

The author was greatly aided in the preparation of this list by Mr. Geo. F. S. Pearce of the Harvard Dental School, who carefully verified each test.

OBSERVED PHENOMENA.	INDICATIONS.
Forms bulky white oxide with active combustion of assay.	Magnesium.
Forms gray coating easily volatilized.	Mercury from amalgams. (See D. II.)
Cherry-red — crimson to black according to amount of substance deposited. Odor of rotten horse-radish; coating not permanent.	Selenium.
White coating or white fumes at very high heat. Assay burns with bluish-white light.	Zinc. (See D. III.)
Silver-white. Assay remains unchanged.	Platinum, metallic.

D. II. *Cover Substance with KI and S. Use Oxidizing Flame.*

OBSERVED PHENOMENA.	INDICATIONS.
Dirty-white and light-gray coating. Treated with fumes of strong NH_3 and again placed in oxidizing flame gives bright-red color. Metallic globule is dull and brittle.	Bismuth.
Dirty white half an inch from assay. Brown directly under assay. No change when treated as above with strong ammonia fumes. Metallic globule is bright and malleable.	Lead.
No coating near assay. Lead-colored, one to one and a half inches, shading to yellow.	Mercury.
Coating bright red when hot, fading to yellow when cold.	Cadmium.
Fine brown coating, very volatile.	Antimony.

D. III. *Examination with Solution of Cobalt Nitrate.*

Heat substance on plaster in the oxidizing flame, moisten well with cobalt nitrate, and again apply oxidizing flame.

OBSERVED PHENOMENA.	INDICATIONS.
Color is deep blue.	Aluminium.
Substance is infusible.	Infusible silicates. (See F.)
Color is fine blue. Substance fusible.	Alkaline silicate, borate, or phosphate.
Color is yellowish green.	Zinc.
Drab to bluish green.	Tin.

D. IV. *Examination with Tetrachloride of Tin.*

OBSERVED PHENOMENA.	INDICATIONS.
Coating pale blue to lavender.	Bismuth.
Coating fine blue, in places almost black.	Antimony.
Delicate pink to red produced only by oxidizing flame.	Neutral and acid chromates.

E. Bead Tests.

The bead tests are made with borax, as described on page 61, or in a similar manner with microcosmic salt, $NaNH_4HPO_4$, which by action of the heat gives up NH_3 and H_2O, becoming sodium metaphosphate, $NaPO_3$. These substances fused on a loop of platinum wire unite with many of the metallic oxides, forming "beads" of various characteristic colors, some of the more important being given below.

With Borax.

Co in the oxidizing flame gives an intense blue bead.
Ni gives a red-brown, yellow when cold.
Cu gives a green, blue, or bluish green when cold.
Cr gives green.
Fe gives a red, yellowish when cold.
Mn gives an amethyst.

With Microcosmic Salt.

Cobalt, copper, nickel, and iron give colors similar to those obtained with borax. Manganese gives a violet bead when heated in the oxidizing flame, but a colorless one in the reducing flame.

F. Special Tests Distinctive or Confirmatory

The oxides of copper and iron may be distinguished by adding a drop of HNO_3, warming gently to drive off excess of acid (high heat will decompose the nitrate, giving the oxide again), and then adding a drop of solution of K_4FeCy_6. Fe will give a dark-blue coloration; Cu will give a brown.

To distinguish between As and Sb stains, add a drop of hypochlorite solution (NaClO). The arsenic stain will dissolve; the antimony stain will remain unaffected (see page 36).

Antimony gives a very characteristic coating on plaster if treated with tetrachloride of tin. The coating is bluish black near assay, fading away to a very delicate color at greater distance. It appears almost immediately and is permanent.

In case of suspected silicates make the " silica skeleton " with a bead of microcosmic salt (page 98).
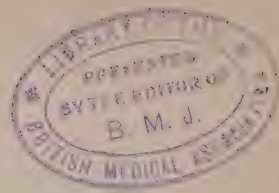
PART II.

DENTAL METALLURGY.

INCLUDING THE CHEMISTRY OF ALLOYS, AMALGAMS, SOLDERS, AND CEMENTS.

CHAPTER XI.

THE METALS.

PROPERTIES OF THE METALS.

METALS are *malleable* in order as follows from gold, the most malleable, to nickel, the least: Au, Ag, Al, Cu, Sn, Pt, Pb, Cd, Zn, Fe, Ni.

Metals are tough or tenacious in order as follows: Fe, Cu, Pt, Ag, Au, Al, Zn, Pb.

The ductility of metals ranges from greatest to least as follows: Au, Ag, Pt, Fe, Ni, Cu, Cd, Al, Zn, Sn, Pb.

Metals conduct heat and electricity in the same order until tin is reached. From tin the order given is correct for heat but not for electricity: Ag, Cu, Au, Al, Zn, Cd, Sn, Fe, Pb, Pt, Bi.

The melting-point of the various metals is of considerable importance in the preparation of alloys. The following table has been compiled from the latest available results. The degrees given are according to the centigrade scale:

Ir.	2200°	Al.		657°
Pt.	1780°	Mg.	500°	(burns)
Ni.	1450°	Sb.		632°
Cast steel.	1300°	Zn.	418°	(burns)
Cast iron.	1200°	Pb.		327°
Cu.	1084°	Cd.		322°
Au.	1075°	Bi.		268°
Ag.	962°	Sn.		232°

If lead, which is the softest of the common metals is taken as a standard and considered as one, the other common metals are harder in the proportion shown in the following table taken from Hall's Dental Chemistry.

Pb......................	1.0	Sb....................	1.8
Sn......................	1.2	Zn....................	1.9
Cd......................	1.4	Pt....................	2.0
Al......................	1.5	Cu....................	2.4
Bi......................	1.6	Fe....................	2.4
Au......................	1.7	Ni....................	2.5
Ag......................	1.8		

The expansion of the various metals under the influence of heat is fairly constant and there have been determined *coefficients of expansion*. These represent the amount of linear expansion of the metals due to a rise in temperature of 1° C., usually from 0° to 1°. The coefficients are not *absolutely* constant, and the amount of expansion observed between 0° and 1° may differ somewhat from that between 50° and 51°. The coefficients vary widely for the different metals; for instance, in passing from 0° to 100° mercury expands 1/16 of its linear measure, copper 1/598, and platinum 1/1123.

Hall's Dental Chemistry gives the following table of expansion from cadmium to platinum (0° — 100°):

Cd..............	1/326	Ag...........	1/518	Ni.............	1/787
Pb..............	1/342	Cu............	1/598	Fe (cast)........	1/934
Zn..............	1/343	Bi............	1/617	Sb.............	1/952
Al..............	1/432	Au............	1/689	Pt............	1/1123
Sn..............	1/448				

According to the kinetic-molecular theory every metal has a certain tendency to pass into solution when immersed in a fluid. If the fluid contains the ions of some other metal of less relative electromotive force the ions in solution will deposit upon the metal, while the metal-ion passes into solution; i.e., the one metal is precipitated by the other. In the list Au, Pt, Ag, Hg, Bi, Cu (Pb, Sn), Co, Cd, each metal precipitates all pre-

ceding it (lead and tin are too nearly alike for either to com-
pletely precipitate the other) and is precipitated by all which
follow. All in the list are precipitated by Zn, Mg, Al, K, and Na.
Iron precipitates copper and the preceding metals but it is
only partly precipitated by those which follow.

The metals are electropositive in the following order from
zinc, the most positive, to gold, the least: Zn, Cd, Fe, Ni, Sn,
Pb, Cu, Bi, Sb, Hg, Ag, Pt, Au; and carbon is negative to all.
It will be noticed that this list of metals is the same, but in
reversed order, and is arranged for the same reason as the list
given in the paragraph above.

Thus if a battery is constructed with zinc as represented in
the cut (Fig. 7), and iron in place of the carbon, then the iron will
be electronegative to the zinc, and hydrogen will be evolved
from its surface; if, on the other hand, iron is
used in place of the zinc, and the carbon remains
as in the cut, the iron will be electropositive to
the carbon, and oxygen will be evolved from its
surface. This property of metals has a direct
bearing upon dental science, because human saliva
may be an exciting fluid for the generation of gal-
vanic currents, its activity being increased by an
abnormal reaction either acid or strongly alkaline,
and it is only necessary to place in the mouth

Fig. 7.

properly related metals, as amalgam fillings or otherwise, to pro-
duce the elements of a galvanic battery.
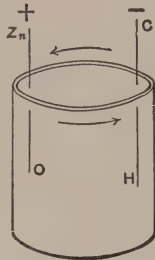
The currents thus generated are, of course, infinitesimal, but
they are constant and may aid in the disintegration of fillings
and in the solution of the constituent metals. Regarding the
extent to which electric currents may exist in the mouth, see
Miller's Micro-organisms of the Human Mouth.

CHAPTER XII.

ALLOYS.

An intimate union of two or more metals, usually produced by fusion, forms an *alloy*. Such a union of one or more metals with mercury is an *amalgam*.

An alloy designed to be used in the preparation of dental amalgams is known as an *amalgam alloy*.

Some metals can be fused together in all proportions, as lead and silver. Others can be made to unite only in limited proportions, as lead and zinc. Lead will carry only 1.6% of zinc, while zinc will unite with only 1.2% of lead. Excess in either case separates out.

The *properties* of an alloy are, as a rule, the modified properties of its constituent metals. An exception to this rule might be made of the sonorous quality of bell-metal and like alloys, this being hardly a property of the constituent metals at all.

Following are some of the more common alloys. The proportions given are general formulæ and may, as a rule, be varied considerably:

Aich's metal,[*] Cu 60%, Zn 38.2%, Fe 1.8%.

Aluminium bronze, yellow, resembles gold, Cu 92, Al 8.

Bell-metal, Cu 80, Sn 20.

Brass, Zn 1 part, Cu 2 parts.

Britannia metal, Cu 2, Sn 82, Sb 16.

Bronze, Cu 65 to 84, Zn from 31.5 to 11, Sn from 2.5 to 4.

Coin silver, Ag 90, Cu 10.

Dental alloys, see page 125.

Dental gold, Cu 85, Zn 15.

* Hepburn.

Dutch metal, Cu 84.5%, Zn 15.5%.

German silver, * Cu 50, Ni 30, Zn 20.

Gun metal, Sn 11, Cu 100.

Mannheim gold, Cu 75%, Zn 25%.

Mosaic gold, Cu 50%, Zn 50%.

Solder, see page 129.

Sterling silver must contain 92.5% Ag.

Type metal, Pb 78, Sb 15, Bi 7.

For fusible metals (Mellot's, Wood's, Rose's, etc.) see page 128.

All alloys (excluding amalgams) are solid at ordinary temperatures with one exception; this one is an alloy of one part potassium with three parts sodium.

The *melting-point* of an alloy is often lower than that of the metals entering into its composition and usually lower than the mean melting-point of its constituents.

In *making alloys* the tendency to separation of the several metals is greater if the alloy is allowed to cool slowly; hence three essentials in the process are: *Complete fusion*, which makes possible *thorough mixing*, and after this has been attained *rapid cooling*. As the fused mass is to be cooled as quickly as possible after fusion is complete, it is desirable to use the least amount of heat practicable in effecting the desired result. To this end fuse first the metal with the lowest melting-point, then add other metals in the order of their melting-points. The more difficultly fusible metal will in a sense dissolve in the more easily fusible metal; an alloy is formed and its temperature has been kept far below the melting-point of the high fusing constituent. This general rule, however, may be modified by the proportion of metal used; thus, in making a silver-tin amalgam-alloy containing 60% of silver it is better first to melt the silver under a flux of carbonate of sodium or borax to prevent superficial oxidation, then add the tin, and lastly any other

* Composition of different samples of German silver may differ widely; some contain about 2.5% of iron and the amount of copper may vary from 40 to 60%.

metal to be used. The *mixing* is attained by stirring with a *wooden* stick and the *cooling* by turning quickly into a cold clean mold. For class work or in making small amounts (twenty grams) of alloy, the Fletcher melting arrangement shown in Fig. 8 is very convenient. The metals are melted in the graphite crucible and then by tipping up the whole contrivance the melted metals flow back into the ingot mold. If the alloy is to be used in the preparation of dental amalgams it must be reduced to fine turnings or filings suitable for ready amalgamation. This is best accomplished in the laboratory by means of a coarse file, the ingot being held by a vise. The fine particles of iron must next be carefully removed with a magnet, and then the filings may be annealed if desired.
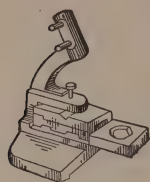
Fig. 8.

The *annealing* of the amalgam-alloys may be accomplished by placing the freshly cut sample in a dry test-tube and keeping the test-tube in boiling water for ten or twelve minutes. It has been claimed that this process is one of superficial oxidation and the changes produced seem to be consistent with this theory. Again, it is claimed that the change is a molecular one of some sort due to change of temperature, and Prof. G. V. Black has shown that an alloy will anneal as rapidly in an atmosphere of nitrogen as of oxygen. The modification of properties produced by annealing varies somewhat with the composition of the alloy; for instance, the liability to discoloration is less in the annealed than in the unannealed sample, if the alloy contains silver and tin, or silver, tin, and zinc, but if copper is a constituent the reverse condition has been found to exist.

It has been shown that the freshly cut amalgam alloys require more mercury for amalgamation than the annealed alloy. The annealed alloy also is slower in setting and contains a smaller proportion of impurities (metallic oxides) which detract from the strength of the amalgam.

Professor Black has shown that while it may be possible to

stop the process of annealing at such a point that a given alloy will neither shrink nor expand, it is easy to carry the process too far and the farther it is allowed to go the greater the shrinkage. It is probably true that the exact effect of annealing will vary with the composition of the alloy, and with different proportions of metals in alloys of the same general composition.

In annealing *platinum* a high degree of heat is required, but the heat should be raised gradually, and in this case, as with gold, the electric furnace furnishes an ideal method.

Eutectic Alloys. — The term eutectic signifies lowest melting-point or freezing-point, and is perhaps best illustrated by water and salt.

If a salt solution, so made that it contains 23.6% by weight of sodium chloride, is cooled to a temperature of − 22° C., the two substances crystallize together in the form of a very intimate mechanical mixture of ice and salt crystals. This is known as a eutectic mixture and these proportions, the eutectic ratio for salt and water.

Upon lowering the temperature of a solution which contains less than 23.6% of salt the excess of water crystallizes in a comparatively pure form, leaving a brine of constantly increasing degree of concentration until the eutectic proportions are reached. If the salt solution were stronger than 23.6% the salt would crystallize out leaving a brine of decreasing concentration. Both of these latter crystallizations however would take place above − 22° C., so the point where the eutectic mixture crystallizes is the lowest possible for a mixture of this particular nature.

In exactly this way a eutectic alloy is one which has the lowest possible melting-point obtainable by use of the given constituents; and in similar manner also, when an excess of one or the other metals is used, we may regard the mixture as a solution of the eutectic alloy in an excess of metal.

The physical differences between the eutectic alloy and " the solid solution " may be shown by microscopical examination,

the eutectic mixture being much more intimate in character than the other. This examination is made by reflected light upon a surface polished as perfectly as possible. The method of procedure is as follows: a thin piece of alloy is polished by the use of emery disks and paper of varying grades until the surface is as smooth as possible, then the polishing is completed by the use of the very finest paper, then by a rapidly rotating wheel covered with cloth upon which jeweler's rouge has been rubbed. The most satisfactory results are obtained if the surface of the alloy is kept wet.

The specimen may be mounted in soft wax contained in a brass ring with perfectly parallel edges, as it is essential that the polished surface be parallel to the microscope stage. After the examination of the polished surface it may be etched by various chemicals such as nitric and hydrochloric acid and again examined.

CHAPTER XIII.

AMALGAMS.

In general, amalgams may be made in three different ways: First, by direct union of the constituents, as in the manufacture of sodium amalgam (page 121); second, by electrolysis of strong solutions of metallic salts in presence of mercury, as in copper amalgam (page 122), and third, by double decomposition as illustrated in the preparation of ammonium amalgam (page 121).

The nature of the amalgam seems to vary with the composition; that is, some amalgams are apparently true chemical compounds, others are solutions of one metal in another, or in mercury, while still others are mixtures of these two, or solutions of the compound; for example silver, gold, and copper will form definite compounds with mercury from which the mercury cannot be separated by heat even at a temperature of 450° C., — nearly a hundred degrees in excess of the boiling-point of mercury, — but these compounds readily unite with larger proportions of mercury in the formation of amalgams. Also platinum, tin, cadmium, and bismuth do not retain mercury at 450° C.; and potassium and sodium form definite crystalline compounds with mercury.

Amalgams possess the peculiar property of " setting " or hardening within a short time after mixing. This in some cases seems to be a process of crystallization, and in all cases is probably due to molecular rearrangement of some sort.

After an amalgam has " set " to a sufficient extent to make it hard to work it may be softened by application of gentle heat. Continued reheating is detrimental to the quality of the

amalgam, and should be avoided; this is particularly true of copper amalgam. It is also possible to sometimes restore the plastic quality of an amalgam by adding a further slight amount of mercury, but the union of the second lot of mercury after the first has partly hardened is very unsatisfactory and results in a weakened product.

Flow of Amalgams. — This property may be defined as the tendency to flatten or change shape under stress or pressure. It is common to most amalgams (copper amalgam being an
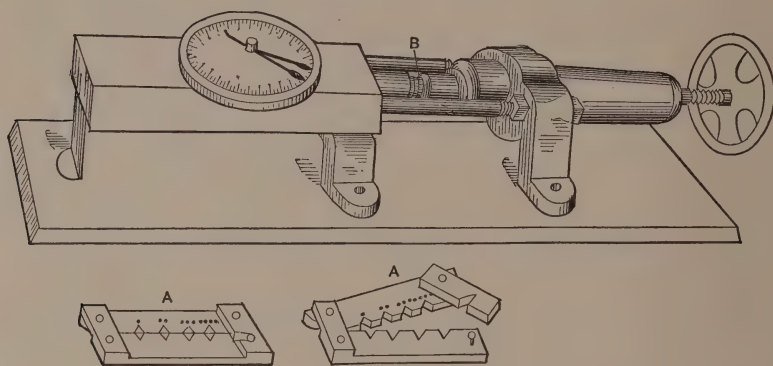
FIG. 9.

exception, according to Dr. Black), and is possessed by many alloys other than amalgams.

Tests for " flow " may be made with the " dynamometer " on cubes of alloy or amalgam measuring one-tenth of an inch each way and the results expressed in percentage of increase or decrease of one dimension. The dynamometer used for this purpose is pictured in Fig. 9 and is a modification of the apparatus devised by Dr. Black and described on pages 408 and 409 of the Dental Cosmos, Vol. 37, *A–A* being the molds in which the cubes of amalgams are set and *B* the point in the apparatus where the cube after setting is introduced with a pair of fine forceps. The dial is supplied with two hands, one which flies

back the instant the cube breaks, the other remaining to indicate the number of pounds applied necessary to crush the cube. The cubes of 1/10 inch are best suited for students' practice, with a dial constructed to record 250 pounds pressure. For accurate comparisons of thoroughly made amalgams the cubes must be made smaller.

Binary amalgams, as they are sometimes called, are those consisting of only one metal besides mercury. These are rarely used in dental practice, but from them the properties of the amalgamated metal are most easily observed.

Sodium amalgam may be made by direct union of the constituent elements. The mercury should be placed in an open dish under a hood, and the sodium added in *small* well-cleaned pieces.

The union is accompanied by a slight hissing noise, an elevation of temperature and evolution of vapor carrying more or less mercury, hence dangerous to breathe. An amalgam containing 1% sodium is a viscid liquid; if it contains 5% sodium it is a hard solid and intermediate percentages give varying degrees of firmness. Sodium amalgam, if made with arsenic-free mercury, is a very convenient reagent to use in making Fleitmann's Test (page 35).

Aluminium amalgam is easily made with aluminium filings and mercury or dilute solution of mercuric chloride. This amalgam decomposes water at ordinary temperatures, giving free hydrogen and aluminium hydroxide.

Ammonium amalgam has no use in dentistry, but it is of interest in that it is the nearest approach which we may attain to the isolation of the purely hypothetical metal ammonium. It is easily made by adding sodium amalgam to a *cold* saturated solution of ammonium chloride, thus illustrating the third general method of preparation of amalgams. It rapidly decomposes at ordinary temperature with the liberation of free hydrogen ammonia-gas and metallic mercury. The hydrogen thus

liberated exhibits the properties of nascent hydrogen, indicating that in the amalgam it existed in true chemical combination, that is NH_4, rather than in any physical solution. At ordinary temperature ammonium amalgam is a soft, pasty, very porous mass, but at much reduced temperature it becomes solid and crystalline, although at $-39°$ (the freezing-point of mercury) hydrogen and NH_3 are still given off.

Copper amalgam is by far the most valuable of this class of amalgams. It may be made by amalgamating precipitated copper after moistening it with nitrate of mercury (Essig). The precipitated copper may be prepared by action of metallic zinc in a slightly acid copper sulphate solution, but must be thoroughly washed with hot water to free it from zinc chloride. The amalgamation may be effected by use of mortar and pestle. Rollins' method * by electrolysis of strong copper sulphate solution is rather unwieldly, but illustrates very well the second general process for the manufacture of amalgams.

Copper amalgam, according to Black, is absolutely rigid after it has once set and does not flow even to a slight extent. It is fine-grained and very hard. It is reduced in strength by reheating and does not expand or contract. In the mouth copper amalgam dissolves with comparative rapidity owing to the ready formation first of copper sulphide, then, by the oxidation of this compound, of the sulphate. It blackens rapidly and in consequence of the tendency just mentioned, to dissolve, it may penetrate the dentine and thus discolor the tooth itself.

Gold amalgam is readily made, but does not, by itself, harden well. An amalgam containing one part of gold to six of mercury will crystallize in four-sided prisms (Litch).

Magnesium amalgam may be easily produced, but like the amalgams with aluminium or sodium it decomposes water with the evolution of hydrogen.

* Details of this method may be found in the Boston Medical and Surgical Journal, February, 1886; also in Mitchell's Dental Chemistry.

Platinum amalgam is very smooth, is formed with difficulty unless the platinum is *very* finely divided, and, like gold, does not harden well.

Silver amalgam, easily made but tends to expand.

Tin amalgam, alone, shrinks badly.

Zinc amalgam, readily made, is white, but too *brittle* to be of service.

Cadmium amalgam may be easily made at ordinary temperature, " sets quickly, and resists sufficiently, but fillings containing it gradually soften and disintegrate and may stain the dentine bright yellow by formation of cadmium sulphide." (Mitchell.)

Effect of Various Metals in Amalgam Alloys.

With the properties of these simpler combinations before us it becomes easy to understand the effect the addition of the various metals will have upon the properties of a silver-tin alloy; for practically *all* amalgam alloys are silver-tin alloys, either simple or combined with one or more other metals.

Silver and tin are the most valuable constituents of amalgam alloys. Silver is essential to the proper setting and hardening of the amalgam. It tends to increase expansion and to hasten setting, while tin possesses the opposite characteristics. Combined with tin in the proportion of 65% silver to 35% tin, it forms an amalgam alloy perhaps more largely used than any other. It was this combination that Dr. Black succeeded in "annealing to zero," that is, so that upon testing it showed neither expansion nor contraction.

Pure silver-tin alloys will flow from 2.5 to 10%.

Dr. C. M. McCauley in an article on amalgams published in the Dental Cosmos for February, 1912, states that the formula of 65% silver and 35% tin will produce an amalgam which gives no shrinkage if the freshly cut alloy is used, but upon annealing the alloy it was necessary to use about 74% silver. He further

states that 5% of copper for an equivalent of silver increases the strength of amalgams made from silver-tin alloys.

Dr. McCauley also tells us that a contraction of one ten-thousandth of an inch will admit organisms producing caries into a tooth cavity, but that the expansion of the finished filling of about one twenty-thousandth of an inch is a desirable result.

The larger the proportion of tin the easier will the alloy cut, but the coarser will be the filings.

Zinc added to a silver-tin alloy tends to whiten the amalgam, hastens setting, increases the flow, and, according to Essig, " causes a great but slow expansion."

Dr. McCauley, quoted above, states that zinc is unfavorable in its action on other metals in a dental alloy and detrimental when used to the extent of only one per cent. because of its tendency to produce a constant expansion for several months, even though tests made during the first few days were satisfactory.

Cadmium, see page 123.

Antimony gives a fine grain alloy and when the silver is less than 50% is supposed to control shrinkage.

Bismuth will increase the flow of the amalgam; it is sometimes used in low-grade silver-tin alloys to control shrinkage.

Copper tends to diminish flow and gives a strength under pressure, sets quickly, gives better margins, and by some is believed to have preservative influence on the tooth substance, but the more copper in an alloy the more rapidly does it discolor.

Gold. — From three to seven per cent. of gold in a silver-tin alloy diminishes shrinkage, helps the color and adds to crushing strength. The filing from such an alloy will be very fine.

Dr. Black says 5% of gold gives a softer working property but retards setting of the amalgam, and makes it otherwise difficult to give a good finish to the filling (Dental Cosmos, Vol. 38, page 988).

Platinum according to Black, is not a desirable addition to a silver-tin alloy. It gives an alloy furnishing *very* fine filing, which produces a dirty working, slow-setting amalgam.

Excess of Mercury. — In the preparation of an amalgam from a dental alloy it is usual to add more mercury than the finished product requires and then squeeze out the excess between the fingers or otherwise. In filling a cavity, still more mercury is forced out, so that the composition of the deeper portions of a filling varies from the outer portions and probably accounts for the inequalities in expansion or contraction. The excess of mercury from the surface of a filling may be absorbed by a little hot gold or pure tin or by finely-divided silver.

Following is a short list of dental alloys, most of which may be easily prepared:

	Sn	Ag	Au	Cu	Zn	Sb
Arington's (S. S. White's)	57.5	42.5				
*(C. A. S.) alloy, C. Ash Sons Co.	27.16	66.54		5.02	0.90	
Chase copper-amalgam alloy	50	50		10		5
Chase's incisor alloy	40	50				10
*Fellowship alloy	26.80	67.45		5.73	0.55	
Flagg's submarine alloy	35	60		5		
Fletcher's gold alloy (old)	56	40	4			
High-grade alloy (7½% gold)	41.5	49	7.5		2	
Harris's amalgam alloy	48.1	40		4.9	7	
King's occidental alloy	54.75	42.75			2.5	
*Odontographic alloy	26.48	66.87	0.28	6.21	trace	
*Standard alloy	35.03	53.55	8.82	2.76		
Standard dental alloy (Eckfeldt)	40.6	52	4.4	3		
60% silver alloy	40	60				
Temporary alloy	88	10			2	
*True dentalloy	27.13	65.91		5.21	1.52	
*Twentieth century	27.13	67.03		4.87	1.10	

* Analyses by Dr. P. J. Burns of the Mass. Inst. Technology, reported in the Journal of the Allied Societies, June, 1908.

These formulæ have been selected from various sources with a view to giving the student opportunity to study effects obtained by varying percentages of tin and silver, and by introduction of other metals, copper, zinc, etc.

The excess of mercury which has to be squeezed out of an amalgam carries with it more or less of the constituent metals. Hall found that whatever the amount of mercury expressed, it carried just about 1% of tin. In the author's experience this amount has reached nearly $1\frac{1}{3}$% of tin. Silver is carried out to a much less extent than tin, so it is not impossible to carelessly make an amalgam and squeeze out enough mercury to change the proportion of silver and tin in the alloy. This change will, of course, be very slight, but we have seen that the contraction and expansion of amalgams may be affected by slight changes in composition.

TESTS FOR AMALGAMS.

Color Test. — This is made upon a freshly amalgamated alloy, rolled into about the shape and size of a small pea, with a view to determine the amount of discoloration the amalgam is liable to undergo in the mouth.

A ball of amalgam carefully smoothed on at least one side is placed for forty-eight hours in a saturated solution of hydrogen sulphide, and after that time its color is compared with other amalgams similarly treated, or with amalgam of a similar composition which has not been treated.

TEST FOR EXPANSION OR CONTRACTION.

Black has shown that tests of this nature to be of any value must be made in such a way that the amount of change in the volume can be measured, and that the simple method of packing glass tubes and using colored ink is wholly unreliable.

The author uses for this purpose an apparatus similar to one described by Prof. Vernon J. Hall. The amalgam is packed closely into a " well " in a steel block, then the block is placed in the apparatus so that a counterpoised steel plunger rests on the column of amalgam. This plunger is operated by a very long needle and attached at a point so near the pivotal support

of the needle that a rise or fall of the plunger of 1/2500 of an inch moves the tip of the needle, at the scale, 1/16 of an inch, or one degree. If the needle rises half a degree, which may easily be read, it would indicate an expansion of the amalgam of 1/5000 of an inch.

There are two wells in each block and both of exactly the same depth. The figure given below will make this explanation easily understood, *A* being the steel block carrying the amalgam.

FIG. 10.

Test for Crushing Strength and Flow. — The test is made with Dr. Black's dynamometer (page 120) upon cubical blocks of amalgam which have been allowed to " set " for at least two days, and which measure 1/10 of an inch each way.

Specific gravity may be obtained by weighing the sample first in water, then in air, and dividing the weight in air by the difference between the two weights obtained.

It is instructive to make these tests on amalgam from alloys of varying composition, also on annealed and unannealed alloys of the same composition.

CHAPTER XIV.

FUSIBLE METALS AND SOLDERS.

FUSIBLE METALS.

Under the head of fusible alloys properly come many of the alloys considered on page 129 as solders. The fusible alloy usually contains lead or bismuth together with tin and occasionally cadmium. This may be mixed in such proportions that the melting-point may be anything desired down to 63° C. These alloys are largely used in the dental laboratory. Mellot's metal, composed of bismuth eight parts, tin five parts, and lead three parts, is perhaps the most serviceable. This melts at about the temperature of boiling water. Wood's metal, melting at about 65° C., is composed of bismuth four parts, tin one, lead two and cadmium one. Rose's metal is bismuth two parts, tin one, and lead one. This melts at about 95° C.

Babbitt Metal, much used in the manufacture of dies, is composed of copper one part, antimony two, and tin eight. The formula of common Babbitt metal on the market will be found to differ somewhat from the above and is not so well suited for dental purposes.

According to Essig's Dental Metallurgy, Dr. C. M. Richmond used a fusible alloy in crown and bridge work which he states is as hard as zinc and can be melted at 150° F. and poured into a plaster impression without generating steam. The formula of this alloy is as follows: Tin twenty parts, lead nineteen, cadmium thirteen, and bismuth forty-eight. The following fusible-metal alloys are also suitable for the purpose.

Tin.	Lead.	Bismuth.	Melting-point of Alloy.
1	2	2	236° F. or 113° C.
5	3	3	202° F. or 94° C.
3	5	8	197° F. or 92° C.

The fusing-point of an alloy may be determined by melting under a liquid of sufficiently high boiling-point and then carefully noting the temperature at which the melted alloy solidifies.

Approximate results may be obtained by watching carefully the melting of a very thin strip of alloy.

Care must be taken that the temperature of the alloy is exactly the same as recorded by the thermometer. To insure this in the case of an alloy with low melting-point, it is usually sufficient to place the alloy in water or brine in a test-tube which is immersed in a beaker of similar fluid, then, by raising the heat gradually with constant stirring and by taking the mean of two or three determinations, fairly accurate results are obtained.

SOLDERS.

Solders are alloys used in joining pieces of metal of the same or of different kinds. One of the constituent metals of the alloy forming the solder is usually the same as the surface upon which it is to be used, hence the various metals re-

FIG. 11.—Apparatus for Taking Melting-Point.

quire solders of special composition; for instance, common solder is entirely unsuited for soldering aluminium or gold.

Common Solder is composed of tin and lead in different proportions. The larger the proportion of tin the finer is the solder, and the following three grades may usually be obtained: " Fine " or "hard " (tin two parts and lead one), " Common " or " medium " (tin and lead equal parts), " Coarse " or " soft " (tin one part and lead two parts).

In soldering metals, it is absolutely essential that the surfaces be kept clean and free from superficial coating of oxides which may form easily with the elevated temperature employed in the process. Soldering acid and the various fluxes serve this purpose. Soldering acid is an acid solution of zinc chloride usually made by taking a few ounces of strong hydrochloric acid and adding zinc as long as the metal dissolves. Among the substances which may be used as a flux to prevent oxidation, rosin and borax are the most common.

Soft Solders are those fusing below a red heat and include the common solders above mentioned, also the most fusible solders containing bismuth. These last are more properly fusible metals and are discussed under that head.

Solders for Aluminium. — Aluminium solders with considerable difficulty owing in part to the low melting-point of the metal, also to the fact that aluminium is attacked by alkalis, including borax, which makes it necessary to find some substitute for this convenient flux. Essig recommends a flux consisting of three parts of copaiba balsam, one part of Venetian turpentine, and a few drops of lemon-juice. The mixture is to be used in the same manner as soldering acid with a solder consisting of zinc from eighty to ninety-two parts, aluminium from eight to twenty parts. Fused and finely powdered silver chloride may also be used as a flux, the salt being reduced and the silver forming a superficial alloy. Richards recommends a solder for aluminium consisting of tin twenty-nine parts, zinc eleven parts, aluminium one part, phosphor-tin one part.

Hall says that a solder which he has found very satisfactory may be prepared from aluminium forty-five parts, tin forty-five, mercury ten; further, that the following formulæ suggested by Schlosser are particularly adapted to soldering dental work since they resist the reaction of corrosive substances.

Platinum-Aluminium Solder.		Gold-Aluminium Solder.	
Gold.............	3. parts	Gold..........	5 parts
Platinum.........	0.1 part	Copper........	1 part
Silver...........	2 parts	Silver..........	1 "
Aluminium.......	10 "	Aluminium.......	2 parts

For soldering articles of aluminium the following solder is given in the Pharmaceutical Era, January 10, 1895: Silver two, nickel five, aluminium nine, tin thirty-four, and zinc fifty parts, to be used without flux. See also Dental Cosmos for 1906 (page 115).

Solder for Brass requires a high heat for fusion and on this account is known as hard solder.

Edwinson gives the following formulæ: (1) copper thirteen parts, silver eleven; (2) copper one part, brass one, silver nineteen; (3) brass five parts, zinc five, silver five. The flux for brass soldering is powdered borax, which may be mixed with water to a paste and applied with a feather or a small brush.

Solder for Gold. — Gold soldering is the most particular work of this class which the dentist has to do. There are a few requirements for a good gold solder which might be noted and which are also applicable to the other solders mentioned: (1) The color should be as nearly as possible that of the metals upon which it is to be used. (2) The solder should have a fusing-point but very slightly below that of the metal to be soldered. (3) The solder should flow freely.

Litch gives the following instructions for making a zinc-gold solder which will have the above-mentioned properties:

" To make the zinc-gold solder take one pennyweight of the same gold upon which it is to be used and add one and a half grains of zinc. If this is done in a crucible in the furnace, first fuse the gold (which should either be clean scraps or be cut from the plate; never use filings for this purpose), using but little borax; when thoroughly fused take the crucible in the tongs, drop the zinc into it, give the crucible a rather vigorous yet

skilful shake to assist in mixing its contents, but without causing any to be thrown out, and immediately pour into the previously prepared ingot mold. This must be done very quickly or the solder will require too high a heat for the fusion on account of a large proportion of the zinc being volatilized or oxidized and thus be lost as alloys."

Essig gives the following formulæ for alloys of gold employed in dentistry as solders:

No. 1. 14 Carats Fine.

American gold coin........	$10.00
Pure silver...............	4 dwts.
Pure copper..............	2 "

No. 2. 14 Carats Fine.

American gold coin.	16 dwts.	
Pure copper......	3 "	18 grs.
Pure silver........	5 "	

No. 3. 14 Carats Fine.

Pure silver...............	2½ dwts.
Pure copper..............	20 grs.
Pure zinc.................	35 "
18-carat gold plate (formula No. 11)................	20 dwts.

No. 4. 15 Carats Fine.

Gold coin..............	6	dwts.
Pure silver............	30	grs.
Pure copper...........	20	"
Brass.................	10	"

No. 5. 16 Carats Fine.

Pure gold............	11 dwts.		
Pure silver...........	3 "	6 grs.	
Pure copper..........	2 "	6 "	

No. 6. 16 Carats Fine.

Pure gold........	11 dwts. 12 grs.
Pure copper......	1 dwt. 12 "
Pure silver.......	3 dwts.
Pure zinc........	12 grs.

No. 7. 18 Carats Fine.

Gold coin..	30 parts	
Pure silver..	4	"
Pure copper.......................................	1 part	
Brass..	1	"

No. 8. 20 Carats Fine, for Crown and Bridge Work.

American gold coin (21.6 carats fine) $10 piece.....	258	grs.
Spelter solder..............	20.64	"

No. 9. 20 Carats Fine, Same Use as No. 8.

Pure gold..	5	dwts.
Pure copper.......................................	6	grs.
Pure silver..	12	"
Spelter solder.....................................	6	"

No. 10. 20 Carats Fine, for Crown and Bridge Work.

Zinc..... .... 1½ grs.
Pure gold.... .... 20 "
Silver solder................................. 3 "

No. 11. Dr. C. M. Richmond's Solder for Bridge Work.

Gold coin...................................... 5 dwts.
Fine brass wire................................ 1 dwt.

No. 12. Dr. Low's Formula for Solder for Crown and Bridge Work, 19 Carats Fine.

Coin gold...................................... 1 dwt.
Copper... 2 grs.
Silver... 4 "

Solder for Platinum. — Platinum utensils may be soldered with any good gold solder, and a flux may be used if desired. When, however, the solder is used in connection with porcelain work, it must be pure gold or a gold and platinum alloy. A twenty-five per cent. platinum alloy has been found to give excellent results. The following in regard to gold and platinum alloy is from the Dental Review, August, 1905:

" The colleges and text-books tell us the proper proportions of gold and platinum alloys, but they usually fail to tell us *how to do it*. In most cases the platinum appears in white spots on the plate without producing a proper alloy. Take a small piece of twenty-two-carat gold and fuse it under the blowpipe. Then work in all the platinum you can in small pieces until it has taken up all that is required. It will produce a small button of a white alloy which is very brittle. Add this alloy in required proportions to the gold in the crucible and it will produce a real platinum alloy. By this method you can make clasp gold that is pretty nearly as stiff as a steel spring and yet will roll and work without fracture." (Mark G. McElhinney, Ottawa, Canada.)

Solder for Silver. — Solder for silver usually consists of alloys of silver and copper with sometimes zinc and sometimes tin. Litch recommends a silver solder made by alloying pure

silver with one-third its weight of brass. " Brannt's Metallic Alloys " gives alloys of silver and copper simply. Hall recommends silver eight parts, copper one, and zinc two. In the preparation of solder containing copper, zinc, or tin, the use of a flux is necessary to prevent the formation of metallic oxide. For this purpose borax is usually employed. The silver, constituting, as it does, the greater proportion of the alloy, should be melted first and be covered with considerable borax. When this has been thoroughly fused, the other metals may be added and mixed by agitation or by stirring with wood. Finally, the solder may be cast in the usual ingot mold.

CHAPTER XV.

DENTAL CEMENTS.

DENTAL Cements may be classified as ordinary oxyphosphates of zinc cements, copper cements and synthetic cements which include the artificial enamels. These three kinds will include by far the larger proportion of cements in common use, and all contain more or less oxyphosphate of zinc.

Oxyphosphate of Zinc. — The oxyphosphate cement is usually made by adding a powder, consisting largely of pure oxide of zinc, colored by a slight amount of other metallic oxides, to a liquid consisting of deliquesced phosphoric acid (or a solution of phosphoric acid in which zinc phosphate, and possibly slight amounts of other phosphates, have been dissolved), till a putty-like mass results, which rapidly hardens and becomes capable of receiving a considerable polish. When the phosphoric acid used is the glacial acid, the cement may be spoken of as a metaphosphate, because the glacial acid, before the addition of water, and to a certain extent afterwards, is actually metaphosphoric acid, HPO_3. The metaphosphoric acid by boiling with water or gradually by addition of water without boiling becomes the orthophosphoric acid (H_3PO_4).

Hall's Dental Chemistry takes the following tests from Flagg's Plastics and Plastic Filling, as characterizing a good oxyphosphate cement.

General Tests. 1. When first mixed it should yield a tough mass which when removed from the spatula does not adhere to the fingers and can be rolled into a pliable pellet.

2. It should have a glassy surface; and, at the end of two or three minutes, it should rebound when dropped upon wood, glass, or porcelain.

3. At the end of five minutes it should be quite hard and should sound like porcelain when tapped.

4. After ten or fifteen minutes it should be dented with difficulty, and when broken should show a clean, sharp fracture.

5. After twenty minutes it should be very hard, and should be capable of taking a good burnish.

6. In thirty minutes it should have little or no acid taste.

Arsenic is a frequent impurity in both zinc oxide and phosphoric acid, and if present is very liable to produce an irritating cement, sometimes causing considerable trouble; hence, the material entering into the composition of any dental cement should be free from arsenic (see pages 34 to 38 for arsenic tests).

The purer the zinc oxide and the phosphoric acid, from which the cement is made, the more durable it is found to be; so, aside from any question of irritation, it is quite necessary for the sake of the cement itself that the ingredients be pure.

It is not intended to give the impression that the liquid should consist *only* of glacial phosphoric acid or the powder *only* of oxide of zinc. A cement thus made would set so rapidly that it would be of no practical value. The resulting mass would also probably be crumbly. The powder or the liquid, one or the other, is usually mixed with phosphates of the heavy metals which would be insoluble in water, but which would dissolve in the strong phosphoric acid.

A pure zinc oxide may be made by calcining the precipitated carbonate of zinc, $Zn_5(OH)_6(CO_3)_2$ + heat = $5 ZnO$ + $2 CO_2$ + $3 H_2O$. The heat should be below 500° F., because, if too strongly heated, the color suffers, becoming yellowish.

Another method of making pure oxide of zinc is given as follows: Dissolve pure zinc in nitric acid, evaporate to dryness,

and heat till fumes cease to be given off. The mechanical effect of the escaping oxides of nitrogen is said to leave the zinc oxide in the form of a *very* fine powder.

A pure phosphoric acid can be made from the ortho-acid by heating till the white fumes begin to come off, then heating to redness, cooling and dissolving in water to a thick syrup. In mixing cements, the powder should be worked into the liquid till the desired consistency is obtained.

Oxyphosphate cement and all cements having zinc oxide for a base tend to dissolve in the fluids of the mouth, lactic acid and ammonium salts being particularly good solvents for this class of compounds. The addition of ferric oxide to oxyphosphate cement increases resistance to disintegration. One part of ferric oxide to six to ten of zinc oxide is recommended by Rollins in the International Dental Journal.

Oxychloride of Zinc is more easily soluble than oxyphosphate. It shrinks more, but is credited with a preservative action on dentine and hence is used to some extent as a lining.

The powder of the oxychloride cement is zinc oxide with sometimes a little borax, or silica, or both, added. A good oxychloride cement will set in fifteen or twenty minutes, but keeps on growing harder for several hours. The following formula is recommended.

Oxide of zinc 10 grams, borax 0.1 gram, and powdered silica, 0.2 gram.

Transfer to clay crucible and calcine for one-half hour in furnace at bright-red heat. Pulverize, sift, and bottle. The liquid to be used with this powder consists of 10 c.c. of pure hydrochloric acid *saturated* with pure zinc and filtered through glass wool.

Oxysulphate of Zinc. — This is used still less than the oxychloride. It is non-irritating, dissolves easily, and is comparatively soft. The following formula is taken from Hall's Dental Chemistry.

Ten grams oxide of zinc, four grams sulphate of zinc. Dry, mix, calcine for one-half hour, and sift.

Liquid to be used with the powder may be made by dissolving two grams of zinc chloride in 10 c.c. of water. This gives a turbid solution and should be shaken when used.

Oxyphosphate of Copper cement (Ames's) consists of the usual powder and liquid. The powder contains oxides of copper, iron (slight amount), cobalt, and zinc, and, of course, is black in color. The liquid is phosphoric acid holding in solution a certain amount of phosphate of zinc.

The cement resulting from this combination was found to be hard, showing practically no change of volume and resisting the solvent action of the saliva.

White Copper cement. The powder of this preparation has been found to consist of 95% oxide of zinc and 5% of cuprous iodide.* The presence of iodine can be easily demonstrated by treatment with nitric acid and the solution of the iodine in chloroform.

Tin cement. Dr. Arthur Scheuer, of Teplitz, Bohemia, recommends a preparation composed of a finely pulverized tin sponge and zinc oxide mixed with glacial phosphoric acid. " The powder is of a light-gray color, becoming slightly darker when mixed with the acid, but regains its original color after setting. A tin-cement filling can be easily inserted and when polished it has a metallic appearance." (Dental Cosmos, May, 1904.)

Artificial Enamel. — Several preparations have been put on the market under this name, in each case with the claim that it makes a much harder cement and one which resists disintegration to a much greater extent than the ordinary zinc preparations.

The specifications of a German patent, under which one of these preparations is manufactured, claim that the powder consists of a mixture of the oxides of beryllium and silicon, together with alumina and lime. The liquid consists of a 50% solution

* W. V. B. Ames, D.D.S., Dental Review, June, 1914.

of orthophosphoric acid in which aluminium phosphate and zinc phosphate have been dissolved.

A qualitative analysis confirms the claim of the patent specifications both in regard to the composition of the liquid and the presence of oxide of beryllium in the powder, and it is probable that the value of these preparations depends largely upon the proportion of beryllium entering into their composition.

This statement from an earlier edition has been quoted * with the assertion that about one-quarter of the powder of Ascher's artificial enamel is beryllium oxide.

Beryllium is a rare metal which occurs naturally with aluminium as a silicate, also as beryllium silicate (beryl), colored forms of which are used as precious stones. Beryllium forms basic compounds of such character as makes it suitable for use in dental cement.

The cement powders may be tested for beryllium as follows: Fuse a little of the powder with sodium carbonate (or the double sodium potassium carbonate); dissolve the fused mass in dilute hydrochloric acid; evaporate to dryness and heat to 120° C. to dehydrate the silica; take up in water with a little hydrochloric acid and filter; to the filtrate (probably containing Al, Be, Zn, and Ca) add a little ammonium chloride, and an excess of ammonium carbonate, $Al(OH)_3$, $Be(OH)_2$, and $CaCO_3$, will be precipitated. The beryllium, however, is easily soluble in the excess of $(NH_4)_2CO_3$. Warm (not boil) and allow to stand for some time to insure complete separation of aluminium.

(*Note.* — $Al(OH)_3$ is much less soluble in solution of $(NH_4)_2CO_3$ than in either NH_4OH or even NH_4OH and NH_4Cl.)

Filter. Boil the filtrate for a long time, when the beryllium and some zinc will be precipitated. Filter and dissolve precipitate off paper in dilute hydrochloric acid. To the filtrate containing $BeCl_2$ and $ZnCl_2$ add NH_4Cl in excess and NH_4OH, which will

* Dental Summary, 1915, p. 56.

give a precipitate of $Be(OH)_2$.   If beryllium and zinc only are present, the separation by boiling may be unnecessary.

The liquid may be tested for dissolved phosphates by diluting with water and adding ammonia till alkaline; if the mixture remains clear, phosphates of alumina, calcium, or zinc are absent.   Care should be used, however, in the addition of the ammonia, as an excess of this reagent will redissolve phosphate of zinc.

If the ammonia is too strong, a precipitate of ammonium phosphate may be obtained, but this may be easily redissolved by the simple addition of water.

Silicate cements, synthetic cements, and synthetic porcelain are names applied to later preparations containing silica, aluminium, and sometimes magnesia in addition to usual cement constituents.   Dr. Ames is authority for the statement that beryllium is useful chiefly for advertising purposes.

It might be well to remember in this connection that the natural sources (ores) of beryllium available in Europe are richer in beryllium than those obtained in this country.

Dr. E. O. Hile, in the Dental Digest for 1913, page 441, says that the production of de Trey's synthetic porcelain is based upon a study of the setting of Portland cement.   The liquid of this porcelain contains a smaller proportion of acid than any cement liquid.

CHAPTER XVI.

RECOVERY OF RESIDUE.

Gold. — The gold scrap may be recovered in two ways: first, by fusion with suitable flux; second, by dissolving in aqua regia and precipitation of the metal. In the first method it is necessary to remove mechanically the impurities as far as possible, then mix the fairly clean gold waste with potassium nitrate and a little borax, and fuse in a clay crucible. The gold will separate as a button at the bottom of the thoroughly fused slag.

In the second method the scrap gold is dissolved in aqua regia and the resulting solution of gold chloride is precipitated with ferrous sulphate or oxalic acid. The latter precipitant, although working more slowly than the iron, does not precipitate platinum, hence in case platinum is present it is the better reagent to use. The precipitated gold is next filtered, thoroughly washed, and fused in clay crucible under borax and potassium nitrate.

Silver. — The recovery of silver is best accomplished by dissolving the scrap or waste in nitric acid and precipitating as chloride, then reducing the chloride to metallic silver either by treatment with pure zinc or by fusion with sodium carbonate. If tin is present in the scrap, the nitric acid will form metastannic acid, a white insoluble powder rather difficult to filter. Hence, it is better to wash this by decantation several times with distilled water, which will remove practically all the silver. From the nitric-acid solution the silver may be precipitated by salt or hydrochloric acid. This precipitate must be washed till the wash-water is practically free from chlorine, then dried and fused

with sodium carbonate, when a button of pure silver will be obtained.

If preferred, the precipitated chloride of silver may be washed once by decantation, then agitated with pure zinc, when the following reaction takes place: .

$$2 \, AgCl + Zn = ZnCl_2 + 2 \, Ag.$$
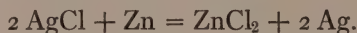
The finely-divided silver (in the form of nearly black powder) must be washed free from chlorine, carefully dried and fused under carbonate of sodium, or, after drying, it may be weighed and dissolved at once if a solution is desired. If the silver residue contains mercury this may be driven off by heat before solution is attempted.

Mercury. — Mercury which has been used in making amalgams is best purified by distillation. Mercury which needs simply to be freed from dirt, dust, or slight traces of other metals may be purified as follows: If a piece of filter-paper is fitted closely in a glass funnel, a pin-hole made in the joint and the paper thoroughly wetted with water and the mercury to be purified placed on the paper, the heavy metal will run through the pin-hole, leaving practically all the dirt clinging to the wet filter-paper. Such mercury may also be cleansed by filtering through chamois-skin.

In case the mercury contains slight amounts of other metals, if it is digested with a very dilute nitric acid, the acid will generally first dissolve the impurities and afterwards a little of the mercury itself. Then thorough washing with water will remove all excess of acid and all soluble salts which may have been formed. Pure mercury should have no coating of any sort on its surface, and if a few globules are allowed to run down a smooth inclined plane, they should leave no " tail " behind.

PART III.

VOLUMETRIC ANALYSIS.

CHAPTER XVII.

STANDARD SOLUTIONS.

VOLUMETRIC analysis is the determination of the quantity of a particular substance contained in a given sample by means of volumetric or standard solutions. By means of standard solutions, it is possible to determine easily and quickly the strength of a peroxide of hydrogen solution, the percentage of silver in an amalgam alloy, or the amount of gold in a plate or solder, and it is volumetric analysis thus specialized and adapted to dental purposes that we shall consider.

The standard solution may be so prepared that it has an arbitrary or special value, such, for instance, as the silver-nitrate solution usually used in determining the amount of chlorine in urine, 1 c.c. of this solution being equal to ten milligrams of salt (NaCl); or its standardization may be made with reference to the molecular weights of the reagents employed, so that solutions of a similar nature will be of equivalent values.

Normal and decinormal solutions, or the volumetric solutions of the U. S. P., are of this character.

A normal solution may be defined as one containing the hydrogen equivalent of the reagent in grams per liter. This definition may be explained by saying that the solution contains the molecular weight of the reagent in grams per liter provided the reagent is of univalent basicity; otherwise such part of the molecular weight is taken as shall represent the molecule reduced to a univalent basicity.

For example, a normal (N/1) solution of hydrochloric acid
or of potassium hydroxide would contain the molecular weight
per liter; one of sulphuric acid or of calcium hydrate would
contain one-half the molecular weight per liter.

If the process involves oxidation, the oxidizing power of the
reagent relative to one atom of hydrogen determines the pro-
portion of the molecular weight to use; for example: iodine (I_2)
and hydrogen peroxide (H_2O_2) will each require half the molec-
ular weight per liter to make a normal solution because in each
case the molecule will " oxidize " two atoms of hydrogen.   So
$K_2Mn_2O_8$, which will furnish five atoms of available oxygen
capable of oxidizing ten atoms of hydrogen, requires only one-
tenth of its molecular weight in 1000 c.c. to produce a normal
solution.

It will be seen from the above explanation that equal volumes
of normal solution will always bring about exact reactions.

The normal solution should not be confused with molar
(M/1) solution used elsewhere in the book, which contains the
molecular weight of the reagent in grams per liter without regard
to the hydrogen equivalent; for example: a molar solution of
H_2SO_4 contains ninety-eight grams, while a normal solution
contains forty-nine grams per liter.

Exact reactions between molar solutions are produced when
volumes corresponding to the respective number of molecules
taking part in the reaction are used.   See Exp. 16, page 371.

The *normal factor* is the weight of reagent contained in *one
cubic centimeter* of the normal solution.

The volumetric process and the use of the normal factor
will be most clearly understood by the explanation of a specific
example.

We will suppose that we have prepared a normal solution of
NaOH and wish to ascertain the strength of a sample of dilute
HCl. The normal solution will contain the molecular weight
in grams of NaOH per liter or forty grams absolute NaOH.

The molecular weight of HCl being 36.4 (36.37), a normal solution of HCl will contain 36.4 grams absolute HCl; and, if a liter of normal NaOH were added to a liter of normal HCl, *exact* neutralization would result:

$$NaOH + HCl = NaCl + H_2O.$$
$$40 \qquad 36.4 \qquad 58.4 \qquad 18$$
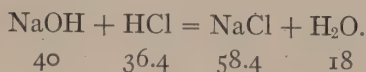
The one liter of normal alkali (containing 40 grams NaOH) is exactly neutralized by 36.4 grams of HCl, or 1 c.c. of normal alkali by 0.0364 gram of HCl. 0.0364 is normal factor of HCl.

Now, if by our process of analysis we find that it takes just 21 c.c. of the NaOH solution to exactly neutralize 10 c.c. of HCl solution, 1 c.c. of NaOH being equal to 0.0364 gram HCl, 21 c.c. of NaOH will be equal to 0.0364 × 21, or 0.7644 gram HCl, or 10 c.c. of the HCl solution contains 0.7644 gram of absolute HCl, equivalent, approximately, to 7.64%.

It has become apparent that in carrying out this process three things are absolutely necessary:

1. Methods for the preparation of standard solutions.

2. Apparatus for *accurate* measurements of both the standard solution and the unknown.

3. Means for determining just when the point of exact neutralization is reached. This point is known as the " *end point* " and is shown by " *indicators* " of various kinds.

Preparation of Standard Solutions. — Experience has shown that normal solutions are in many cases less convenient to work with than those much more dilute, both on account of the keeping qualities of the standard solution and the accuracy of manipulation; and, for the purposes of dental chemistry, a *decinormal* or one-tenth normal solution represented by N/10 will generally be used.

In working with an N/10 solution, the factor used in calculations of results will be one-tenth of the normal factor and

is termed an N/10 *factor*. Other fractional proportions of the normal solution may be used as the centinormal, N/100, or seminormal, N/2. While the decinormal solution contains one-tenth of the hydrogen equivalent of reagent in grams per liter, and this amount is very easy to calculate, it is often very difficult to *weigh out* the exact amount required. For instance, we want an N/10 solution of HCl. HCl is a gas soluble in water and the strengths of the solutions vary greatly, so we cannot weigh out 3.637 grams of absolute HCl to put in 1000 c.c. of water though we know this is just the amount necessary to produce our N/10 solution. Thus, one of the first practical difficulties in making up standard solutions is to find some substance which can be weighed accurately and the exact chemical composition of which may be relied upon.

Crystallized oxalic acid is such a compound, although care must be taken that the crystals are dry and yet contain all their water of crystallization; in other words, are actually represented by the formula $H_2C_2O_4,2\ H_2O$. Fused carbonate of sodium is another such compound. If the purest obtainable bicarbonate of soda is fused till no further change takes place, cooled, and powdered, the product is pure enough for the preparation of a standard solution for ordinary use.

For the preparation of volumetric solutions it is necessary to have a balance which will weigh accurately to at least two decimal points. It will be much better to have a balance sensitive to one milligram. Balances of this sort inclosed in a glass case can be obtained at a very reasonable price. Fig. 12 on page 147 represents such a balance.

It is also essential to have flasks capable of holding 100, 250, 500, and 1000 c.c. carefully graduated on the neck, represented in Fig. 13, page 147.

Graduated cylinders (Fig. 14) are not so well suited for the preparation of standard solutions, as the greater breadth of the column of liquid makes accurate reading much more difficult.
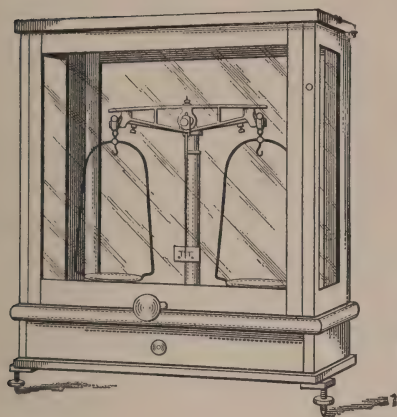
FIG. 12.
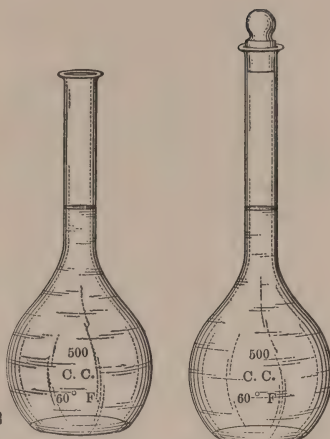
FIG. 13.

FIG. 14.

FIG. 15.
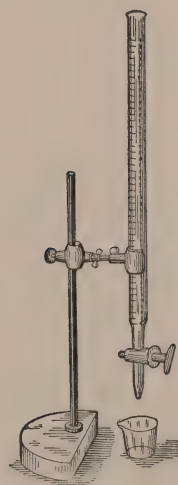
FIG. 16.

Small cylinders of 100 c.c. or less are useful in making up odd amounts of solution.

In the process of analysis it will be necessary to have pipettes (Fig. 15) measuring 5 and 10 c.c., also a burette (Fig. 16), from which the standard solution may be used. The burettes may be had in a variety of styles and sizes, a very serviceable one being of 25 c.c. capacity and graduated in tenths of a cubic centimeter. It may have a glass stop-cock or it may be furnished with a glass tip with rubber connector and pinch-cock.

A set of measuring-instruments which have been carefully compared with one another should be kept; that is, the 1000-c.c. flask should be exactly filled by taking the 100-c.c. flask full to the mark just ten times, thus enabling one accurately to take aliquot parts of any given solution.

INDICATORS.

The third requisite for carrying out a volumetric process is a method for determining the end point of the reaction; that is, we must know when there has been a sufficient quantity of a standard solution added to an unknown solution. *Phenolphthalein* gives a red color with alkalis, which is discharged by the addition of acid till the solution becomes colorless as it becomes neutral or acid. *Litmus* gives a blue color with alkalis and a red with acids; *Methyl orange* can be used with carbonates and mineral acids; it does not work so well with organic acids. The color is pink in acid and yellow in alkaline solution. *Lacmoid* is useful in cases where the acid properties of such salts as alum or zinc chloride might interfere with the use of litmus or phenolphthalein. The different indicators do not all change color at exactly the same point in the process of neutralization, and it is possible for a solution to be alkaline to litmus and acid to phenolphthalein at the same time. Hence uniformity in the use of indicators is desirable. In physiological

chemistry, congo red, tropæolin *oo*, and dimethylaminoazoben-
zene are also used.

The end point may be indicated by excess of a standard
solution if it happens to be highly colored, as potassium per-
manganate. Thin starch paste is used as an indicator in oper-
ations involving the use or liberation of free iodine. Other
indicators will be considered as we have occasion to use them in
the various analytical processes.

The processes of volumetric analysis may be divided into
three classes: First, *acidimetry* and *alkalimetry*. Second, *oxi-
dation* and *reduction*. Third, *precipitation*.

ACIDIMETRY AND ALKALIMETRY.

Acidimetry and alkalimetry includes all standardized solu-
tions, either acid or alkaline, which may be used in neutralizing
solutions of unknown strength of an opposite character. For
instance, the strength of vinegar is determined by neutralizing
a known volume with standard alkali.

For present purposes two standard acids and one standard
alkaline solution will be sufficient.

DECINORMAL OXALIC ACID.

The first of these may be decinormal oxalic solution prepared
from recently recrystallized and carefully dried acid. The
composition of these crystals should be $H_2C_2O_4.2 H_2O$, having
molecular weight of 126.

If we consider the reaction involved in the neutralization
of oxalic acid ($H_2C_2O_4 + 2 NaOH = Na_2C_2O_4 + 2 H_2O$) we see
that twice as much alkali is required as would be necessary to
neutralize a monobasic acid like HCl. Hence to obtain our
hydrogen equivalent we divide the molecular weight of oxalic
acid by two, which will give us a weight in grams to be dis-

solved in sufficient water to make one liter of normal solution. A decinormal solution will be one-tenth of this strength.

For class use, each student may prepare 500 c.c. of this solution by dissolving 3.15 grams of pure crystallized oxalic acid in water and dilute to a half-liter. The graduated flasks are usually constructed to be used at a temperature of 60° F. or 15° C. and for accurate work solutions must be brought to this temperature. After the oxalic acid solution has been prepared the decinormal alkali may be made as follows:

DECINORMAL SODIUM HYDROXIDE.

Weigh out carefully two and a half grams of caustic soda or three grams of caustic potash and dissolve in less than 500 c.c. of distilled water. After the solution has thoroughly cooled, fill a burette with it. Place 10 c.c. of standard acid previously prepared in a white porcelain dish of about 250 c.c. capacity, add 20 c.c. distilled water and two or three drops of phenol-phthalein (2% phenolphthalein in alcohol and water, equal parts); then carefully run in from the burette, with constant stirring, the alkali solution until a permanent pink tint is produced. This process is known as " titration," and will hereafter be so designated.

The work will be more satisfactory if the titration is made for the appearance of color rather than the disappearance of color, as would have been the case had the standard acid run *into* the measured alkali solution.

The Calculation. — Supposing it has taken 8.2 c.c. of the alkali to exactly neutralize the 10 c.c. of N/10 acid, it follows that in the 8.2 c.c. there is sufficient alkali to equal or to make 10 c.c. of an N/10 alkali solution; hence we may add 1.8 c.c. of distilled water to every 8.2 c.c. of alkali solution, thereby reducing it to decinormal strength. Practically we should take 410 c.c. of alkali solution and in a graduated flask make it up to 500 c.c. with distilled water. It will be necessary to make

several titrations and average the results before making the calculation.

From the standard alkali N/10 solutions of HCl or H_2SO_4 may be prepared in a similar manner, it being impossible to accurately weigh either of these two acids. In titrating a carbonate, if an indicator, such as phenolphthalein, which is sensitive to carbonic acid, is used, it is necessary to keep the solution at a boiling temperature or at least bring it to a boil after every addition from the burette.

VOLUMETRIC DETERMINATION OF ACETIC ACID.

As an example of acidimetry and alkalimetry determine the strength of a sample of vinegar as follows:

Measure accurately into a white porcelain dish of 150–250 c.c. capacity 1 c.c. of the sample. This may be measured either with a carefully graduated 1-c.c. pipette or more accurately by diluting 10 c.c. of the sample to 100 c.c. in a graduated flask, then using 10 c.c. of the dilution for the titration, the titration to be performed with N/10 NaOH, using phenolphthalein as an indicator.

The molecular weight of acetic acid is, in round numbers, 60; hence the N/10 factor of acetic acid will be 0.006 (acetic acid being monobasic, $HC_2H_3O_2$). To ascertain the strength of the sample of vinegar it is necessary to multiply the number of cubic centimeters used by this factor, 0.006, which will give the amount of absolute acid calculated as acetic in 1 c.c. (practically 1 gram) of the sample. Thus, if 8 c.c. of N/10 alkali were required to neutralize 1 c.c. of vinegar, multiplying the factor 0.006 by 8 would give 0.048 gram of absolute acetic acid in 1 c.c. of vinegar, which is equivalent to 4.8%.

VOLUMETRIC SOLUTION OF HYDROCHLORIC ACID.

The volatile character of hydrochloric acid renders a solution of normal strength rather unstable, so decinormal or weaker

solutions of this acid are commonly employed.   Take a solution
of hydrochloric acid which shall contain four to four and one-half
grams per liter.   Make several titrations with decinormal so-
dium hydroxide and from the average of these dilute to decinor-
mal strength as follows: the acid solution has been made rather
stronger than decinormal so the 10 c.c. of dilute HCl may have
required 12.5 c.c. of standard alkali for exact neutralization.   In
this case add 250 c.c. of distilled water to 1000 c.c. of the acid.

DETERMINATION OF MAGNESIUM HYDRATE OR MILK OF MAGNESIA.

The strength of milk of magnesia may be volumetrically
determined as follows: To five grams of carefully mixed and
accurately weighed milk of magnesia add twenty-five cubic
centimeters of normal sulphuric acid.   When dissolved, dilute
the solution to 250 c.c.   Mix thoroughly and titrate 25 c.c.
of this solution with decinormal alkali.   The result of this
titration multiplied by ten will give the uncombined acid.
Subtract this from the volume of standard acid originally used
and calculate the amount of $Mg(OH)_2$.   Each cubic centimeter
of the normal acid corresponds to 0.02917 gram of magnesium
hydroxide.

Note. — This process is based upon the last revision of the United States
Pharmacopœia in which the term cubic centimeter is everywhere replaced by the
name mils.   This term indicates a milliliter or one-thousandth of a liter, which the
revisers consider to be more accurate than cubic centimeter.

CARBONATE TITRATION.

While perhaps phenolphthalein is the most serviceable of all
indicators in common use, it is so sensitive to carbon dioxide that
any titration which results in the liberation of CO_2 must be
modified by boiling the solution thoroughly after each addition
of acid.   This makes the operation somewhat tedious, but it is
to be preferred to the use of other and less sensitive indicators
which may not be affected by the carbon dioxide.

Analysis by Oxidation and Reduction.

DECINORMAL PERMANGANATE OF POTASSIUM.

If to a hot solution of oxalic acid containing sulphuric acid, permanganate of potash be added, the following reaction takes place:

$$2 \; KMnO_4 + 5 \; H_2C_2O_4 + 3 \; H_2SO_4 = K_2SO_4 + 2 \; MnSO_4 + 10 \; CO_2 + 8 \; H_2O.$$
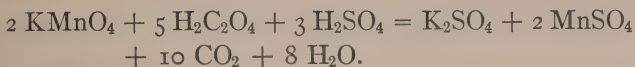
This reaction represents a very valuable method of volumetric analysis; but, inasmuch as it is not a process of neutralization, it cannot properly come under the head of acidimetry and alkalimetry, but rather under a distinct classification, the determination involving *oxidation* and *reduction*.

Standard Permanganate Solution. — In the reaction given above we may consider that, as the molecule of $K_2Mn_2O_8$ breaks up, three of the eight atoms of oxygen are required to form the basic oxides K_2O and $2 \; MnO$ (soluble in the acid as K_2SO_4 and $2 \; MnSO_4$), while the remaining five atoms are liberated and constitute the active chemical agent whereby the oxalic acid is oxidized to CO_2 and H_2O. Hence, to reduce this double molecular weight (316) to the hydrogen equivalent necessary for a normal solution, it is divided by 10 (five atoms of oxygen having a valence of 10).

The Decinormal Solution may be made by dissolving 3.16 grams of pure recrystallized and thoroughly dried crystals, if they can be obtained, in distilled water, and making the solution up to 1000 c.c., or it may be standardized by titration with the N/10 oxalic acid previously prepared; in this case one would proceed as follows:

Make a solution slightly stronger than the standard required, say about 3.5 grams of the ordinary pure crystals in a liter of water; with this fill a burette, place 10 c.c. of N/10 oxalic acid measured from a pipette in an evaporating-dish or casserole, dilute with about 50 c.c. of water, add about 10 c.c. of dilute

sulphuric acid, and heat the mixture nearly to the boiling-point. Then titrate with the permanganate from the burette. The permanganate will at first be rapidly decolorized, but as the operation progresses the color fades more slowly till at last a faint *permanent* pink color indicates that the " end point " has been reached.

The temperature must be kept above 60° C. throughout the titration or the oxidation will take place too slowly and an apparent end point will be obtained before the reaction is completed.

If the solution turns muddy during the operation, it is due to an insufficient amount of sulphuric acid and more should be added. The calculation is made as in the case of the N/10 NaOH described on page 150. The standard permanganate should be preserved in full, well-stoppered bottles and kept in a dark place.

It is better to have the $KMnO_4$ solution made up a day or two before it is standardized, thereby allowing for oxidation of traces of ammonia, etc., which the water may contain.

DETERMINATION OF PEROXIDE OF HYDROGEN.

In determining the strength of peroxide use 1 c.c. of the sample measured, as in the case of vinegar (which see), dilute with 50 c.c. of distilled water, add 10 c.c. of dilute sulphuric acid, and titrate with the permanganate in exactly the same manner as detailed in the preceding paragraph, with the exception that the titration must be made cold. The reaction takes place so easily that heat is unnecessary and even a slight elevation of temperature may result in loss of hydrogen peroxide, the reaction in this case being as follows:

$$2 KMnO_4 + 5 H_2O_2 + 3 H_2SO_4 = K_2SO_4 + 2 MnSO_4 + 5 O_2 + 8 H_2O.$$
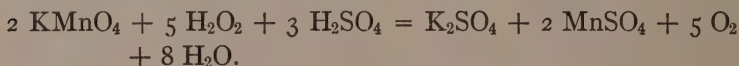
The aqueous solutions of peroxide on the market used as

antiseptics contain about 3% absolute H_2O_2 and yield approximately ten volumes of available oxygen; that is, 10 c.c. of solution will yield 100 c.c. of oxygen. The calculation may be made to express strength of the peroxide in terms of percentage of absolute H_2O_2 by multiplying the number of cubic centimeters of $N/10$ $KMnO_4$ decolorized by 1 c.c. of solution by 0.17, or to express the strength in volumes of available oxygen by multiplying the number of cubic centimeters of solution by 0.56 (more accurately 0.5594).

DECINORMAL IODINE

A decinormal solution of iodine may be prepared by dissolving 12.68 grams of pure iodine crystals in one liter of water by the aid of about 18 grams of pure potassium iodide.

Iodine of sufficient purity may be obtained by carefully resubliming selected and carefully dried crystals of so-called " chemically-pure " iodine.

DECINORMAL SODIUM THIOSULPHATE.

$Na_2S_2O_3.5\ H_2O$, molecular weight = 248.24. This solution may be made by weighing directly 24.824 grams of the pure crystallized salt, dissolving in water and diluting to 1000 c.c., or it may be standardized by titration with a decinormal iodine solution, the reaction being as follows:

$$2\ Na_2S_2O_3 + 2\ I = 2\ NaI + Na_2S_4O_6.$$
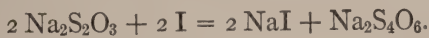
The indicator used is a very dilute starch paste, which gives the characteristic blue color as soon as free iodine is in excess.

By means of these two standard solutions (iodine and sodium thiosulphate) a variety of determinations may be made with great accuracy. Any substance which will liberate iodine from potassium iodide may be quantitated by adding an excess of the potassium salt and titrating the free iodine with thiosulphate solution, using starch paste as usual for an indicator.

Peroxide of hydrogen may be thus determined as easily as

by the permanganate method previously given. The process, being that of Kingzett, is given as follows by Sutton:

Mix 10 c.c. of peroxide solution to be examined with about 31 c.c. of dilute sulphuric acid (1–2) in a beaker, adding crystals of potassium iodide in sufficient quantity, and after standing five minutes titrating the liberated iodine with $N/10$ thiosulphate and starch. The peroxide solution should not exceed the strength of two volumes; if stronger, it must be diluted proportionately before the analysis.

In the case of a very weak solution it will be advisable to titrate with $N/100$ thiosulphate.

1 c.c. $N/10$ thiosulphate = 0.0017 gram H_2O_2.

DETERMINATION OF IODINE SOLUTION.

Titrate 10 c.c. of the iodine solution with standard sodium thiosulphate until the iodine color has become a pale yellow; then, and not until then, add the starch paste indicator and continue titration until blue color is discharged.

DETERMINATION OF HYPOCHLORITE SOLUTION.

By the use of sodium thiosulphate the strength of chlorinated lime, used as a disinfectant, may be easily determined. The following process is based upon the assay given in the nineteenth revision of the Pharmacopœia (1916).

Into a small, tared, stoppered, weighing bottle containing 10 c.c. of distilled water introduce about two grams of chlorinated lime and weigh carefully. In a small mortar rub this mixture with repeated portions of water which are to be carefully transferred to a 500-c.c. graduated cylinder. When one or two hundred c.c. of water have been used in this way rinse the weighing flask and mortar several times with distilled water, adding the rinsings to the graduated cylinder, and finally making the entire volume measure exactly 500 c.c. Mix thoroughly

and allow to settle. Take twenty-five to fifty c.c. of this mixture accurately measured, transfer to a porcelain dish, add half a gram of potassium iodide and two to three c.c. of acetic acid and titrate with decinormal sodium thiosulphate solution, using dilute starch solution as an indicator. Each cubic centimeter of the standard thiosulphate corresponds to 0.003546 of a gram of available chlorine.

Note. — The strength of metallic peroxides may be determined by acting upon the peroxide with hydrochloric acid, conducting the liberated chlorine into a potassium iodide solution and titrating the liberated iodine with standard thiosulphate.

VOLUMETRIC DETERMINATION OF ARSENIC.

Mohr's method of oxidation with iodine is a practical one. The titration is made with $N/10$ iodine and starch as usual, except that the solution should be at first neutral and then about 20 c.c. of saturated solution of sodium bicarbonate should be added to every 0.1 gram of As_2O_3 supposed to be in the unknown, thus giving a certain definite alkalinity. If the solution is acid, neutralize with sodium bicarbonate, then make alkaline with more bicarbonate as above.

VOLUMETRIC DETERMINATION OF GOLD.

While gold is usually determined quantitatively by assay in a dry way (page 164) it may be determined very accurately by titration with thiosulphate solution. Fatka (Chem. Zeit.) recommends the following process based upon the fact that a neutral solution of gold salt with potassium iodide will give a greenish precipitate. When an excess of potassium iodide is used no precipitate is formed, but a solution of AuI_3 as $AuKI_4$ results. This is of a brown color and may be titrated with $N/10$ thiosulphate solution, when the following reaction takes place:

$$AuKI_4 + 2\,Na_2S_2O_3 = AuKI_2 + 2\,NaI + Na_2S_4O_6.$$

Process: 10 c.c. of gold solution containing approximately 2% of gold is treated with 4 grams of potassium iodide diluted to 100 c.c. with water and titrated with $N/10$ $Na_2S_2O_3$ solution, using starch as an indicator.

VOLUMETRIC DETERMINATION OF GOLD.
(Second Method.)

In the analysis of dental alloy, gold will remain undissolved by HNO_3 and will be weighed with the SnO_2. It should be separated and its weight deducted before calculation is made for tin. This may be done by dissolving the gold in dilute aqua regia, evaporating the solution of gold chloride to dryness, dissolving residue in distilled water and proceeding according to following method from Schimpf's Manual of Volumetric Analysis.

The gold must be in the form of chloride ($AuCl_3$).

To the solution of gold chloride a measured excess of $N/1$ oxalic acid solution is added and the mixture set aside for twenty-four hours.

The solution is then made up to a definite volume (say 300 c.c.). Then, by means of a pipette, 100 c.c. are removed, and the excess of oxalic found by titrating with $N/10$ permanganate in the presence of sulphuric acid. The reaction is

$$2\,AuCl_3 + 3\,H_2C_2O_4 = 2\,Au + 6\,HCl + 6\,CO_2.$$
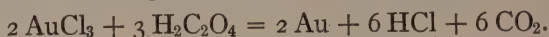
Each cubic centimeter of $N/1$ oxalic acid solution = 0.06523 gram of Au, or 0.1004 gram of $AuCl_3$.

ANALYSIS BY PRECIPITATION.

Because certain elements possess a selective affinity for other elements it is possible to determine many substances quantitatively by precipitation. That is, if silver nitrate is added to a mixture of a soluble chloride and a chromate, the chlorine will combine first with the silver, forming AgCl, to the exclusion of the chromate. After the last trace of chlorine has

been so combined, the silver chromate will be formed, which is a salt with an intense red color; hence it is possible to determine the strength of solutions of soluble chlorides by titration with standard $AgNO_3$, using potassium chromate as an indicator. This process is used in analysis of drinking-water, of saliva, and of urine, but for each of these it is desirable to have solutions of special strength.

A DECINORMAL SILVER SOLUTION

may be made by dissolving seventeen grams of pure crystallized $AgNO_3$ in a liter of distilled water, and with this a

DECINORMAL SODIUM CHLORIDE SOLUTION

may be prepared as follows:

Weigh out six grams of the purest salt obtainable and dissolve in approximately one liter of distilled water. With a pipette measure 10 c.c. of this solution into a white porcelain dish, dilute to about 20 c.c. with H_2O, add two to five drops of neutral potassium chromate (K_2CrO_4) and add $AgNO_3$ from a burette till a faint pink color *persists*.

The calculation and dilution is made exactly as described on page 150 in the preparation of a standard NaOH solution. The silver nitrate solution used to determine chlorine in urine may be prepared of such a strength that 1 c.c. precipitates just 10 milligrams of sodium chloride. This is equivalent to 0.006065 gram of chlorine. A solution of this strength is produced when 29.075 grams of pure, fused silver nitrate are dissolved in sufficient distilled water to measure one liter of solution. If chlorine is to be determined in drinking-water, it is usually necessary to concentrate the water to at least one-fifth its bulk and then to use not more than one or two drops of neutral chromate as indicator. The standard silver nitrate for this titration should be very dilute. A convenient solution may be prepared

by diluting the standard AgNO$_3$ for urine 1 to 10. In saliva the sample may be diluted with an equal volume of water and titrated the same as in the case of drinking-water. In all quantitative processes where silver chromate is used to determine the end point the solution must be practically neutral, as the formation of this salt is prevented by either acids or alkalis.

DECINORMAL POTASSIUM SULPHO-CYANATE.

This solution may be made in a manner similar to that previously described for the preparation of standard sodium chloride solution, except that a fairly strong solution of ferric alum should be used as indicator and the titrated solution should contain moderate excess of nitric acid.

DETERMINATION OF SILVER BY SODIUM CHLORIDE SOLUTION.

The strength of neutral silver solutions may be determined by the use of decinormal sodium chloride using yellow potassium chromate as an indicator. It is better to add the silver solution from the burette as the precipitate of silver chromate which would be formed by adding the indicator to the silver solution disintegrates with difficulty.

DETERMINATION OF SILVER BY POTASSIUM SULPHO-CYANATE SOLUTION.

Silver may be determined volumetrically in nitric acid solution by titration with standard KCNS solution, using ferric alum as an indicator. The sulphocyanate solution must be standardized against decinormal AgNO$_3$ as follows: Prepare a solution containing not less than 10 grams of chemically pure KCNS per liter. Place this solution in the burette and put in the porcelain dish 10 c.c. of decinormal AgNO$_3$ which has been strongly acidified with nitric acid and fifteen or twenty drops of

a solution of ferric alum, added as an indicator. The end point is indicated by the faint red color of ferric sulphocyanate, produced by the first excess of KCNS. The calculation will be the same as previously described in the preparation of N/10 NaOH (page 150).

DETERMINATION OF CHLORINE IN URINE.

A rough determination of chlorine may be made by titrating 10 c.c. of urine with standard silver nitrate, using potassium chromate as an indicator (see page 159). An accurate determination may be made by acidifying 10 c.c. of urine with nitric acid. Add 20 c.c. of decinormal silver nitrate solution and titrate the excess of silver nitrate by using standard KCNS with ferric alum as an indicator. (In this case the presence of a considerable quantity of silver chloride makes it unnecessary, and in fact impracticable, to use the silver solution in the burette.) Subtract the number of c.c. of N/10 AgNO$_3$ used for this titration from the 20 c.c. at first added and the remainder represents the chlorine content of the urine.

VOLUMETRIC DETERMINATION OF COPPER.

Into a solution of copper, free from other metals of Group I or II, pass H$_2$S gas. Wash the resulting copper sulphide thoroughly with H$_2$S water, and dissolve in dilute nitric acid; then wash the paper in warm water, add to the filtrate (wash water) sodium carbonate until precipitate formed is nearly dissolved; then add 1 c.c. of dilute NH$_4$OH. Titrate, to complete disappearance of blue color, with KCN solution previously standardized after this same method against pure copper wire. A little practice is required in determining the end point to give the process any degree of accuracy. An excess of ammonia should be avoided, as it interferes with the accuracy of the end point.

VOLUMETRIC DETERMINATION OF ZINC.
(For use in analysis of amalgam alloys.)

The solution from which silver and copper have been removed, together with all wash-water, may be concentrated; if acid in reaction it should be evaporated to dryness, and the residue dissolved in water; then add a fairly strong solution of oxalic acid and an equal volume of strong alcohol. Allow to stand 15 to 30 minutes, filter, and wash with 70% alcohol till oxalic acid is removed, dry until the alcohol has disappeared, dissolve in dilute sulphuric acid, and titrate the solution with $N/10$ permanganate and calculate the zinc from the amount of oxalic acid found.

This method is usually fully as satisfactory as the gravimetric determination given on page 165.

VOLUMETRIC DETERMINATION OF CALCIUM.
(For use in saliva analysis.)

This method is based upon that recommended by Dr. Percy R. Howe, Dental Cosmos, April, 1912. To 5 c.c. of saliva, add as much more distilled water and a slight excess of oxalic acid or ammonium oxalate (5 c.c. of normal solution will be sufficient). Add ammonium water to alkaline reaction, heat nearly to the boiling point, and allow to stand for twenty to thirty minutes. Filter through a hardened filter paper into a small beaker which is allowed to stand on a piece of black glazed paper. Under these circumstances, a slight rotary motion of the beaker will show if any of the white precipitate of calcium oxalate is passing through the paper.

After filtration is complete, wash five times in hot distilled water; then place the precipitate, together with the paper, into a small beaker, add about 30 c.c. of dilute sulphuric acid, and heat nearly to the boiling point; then titrate with $N/20$ permanganate solution.

GRAVIMETRIC DETERMINATIONS.

Gravimetric determinations are, as a rule, more accurate than volumetric; but they require greater care and attention to details, making them less satisfactory in the hands of the beginner. Some determinations, however, on account of difficulties in obtaining accurate end points and absolute separations, are really easier when made by gravimetric processes. A few of these will be given.

GRAVIMETRIC DETERMINATION OF TIN AS SnO_2.

Tin may be separated from dental alloys in the absence of gold or platinum by simply dissolving the alloy in nitric acid. Tin will remain as a white insoluble metastannic acid. " As stated on page 40 metastannic acid, upon long standing, will change to somewhat soluble compounds, hence this operation should be completed with reasonable rapidity. After complete disintegration of the alloy, the insoluble tin compound may be separated by filtration through asbestos fiber, contained in a Gooch crucible. The method of procedure is as follows:

A little fine asbestos fiber, washed in acid and held in suspension in water, is placed on the bottom of the crucible. The crucible is then placed in the top of a filtering flask from which the air is exhausted by the suction pump. This packs the asbestos down firmly on the bottom of the crucible in a thin layer, and care should be taken that the quantity of asbestos used is such that water will pass through it easily. The crucible with asbestos is next dried, ignited, and weighed. Now transfer the precipitate of tin oxide (metastannic acid) to the crucible, taking care that none is lost, and wash thoroughly six or eight times, then dry, ignite strongly, and weigh again.

If the ignited residue, weighed as tin oxide, does not contain gold or platinum, the weight of tin may be obtained by multiplying the weight of the ash by 0.788.

GRAVIMETRIC DETERMINATION OF SILVER.

The gravimetric determination of silver is not difficult, and is rather more accurate than the volumetric method. The silver is obtained in the form of silver chloride. This is separated by filtration through an ashless paper, and dried. Then the dried precipitate is removed as completely as possible onto a square of black glazed paper and preserved under a funnel or bell glass. The filter paper, containing traces of silver chloride which could not be removed, is next incinerated in a previously weighed porcelain crucible.

As slight reduction of silver chloride to silver may take place during the ignition of the paper, it is necessary to add, after the paper is completely burned, a drop or two of nitric acid, and after the excess has been driven off by gentle heat, a drop or two of hydrochloric acid. This treatment dissolves any reduced silver and precipitates silver chloride. After carefully heating to dry the precipitate in the crucible, the reserved portion of silver chloride is carefully brushed into the crucible, and the whole ignited until the silver chloride begins to fuse. It is then cooled and weighed as silver chloride.

GRAVIMETRIC DETERMINATION OF COPPER.

Copper may be determined quite easily by electrolysis of the faintly acid (H_2SO_4) solution. The copper solution must be freed from other metals and preferably be obtained as a solution of copper sulphate of approximately 0.1 of 1% of copper. 50 c.c. of such a solution are put into a platinum dish which is placed upon a copper plate connected with the negative pole of a battery. A strip of platinum suspended from the positive pole is immersed in the solution and the current allowed to pass for from three to twelve hours, according to the strength of the copper solution. The ordinary 110-volt (direct) current employed for electric lighting may be used by introducing a re-

sistance of from three to six 40 watt lamps. After the copper has been entirely deposited the residual solution is drained out of the platinum dish, a little alcohol added, which is also drained out, and by setting fire to the last traces of alcohol the precipitated copper is dried and in condition to weigh. Care must be taken to avoid oxidation of the finely-divided copper; if it turns black too much heat has been used and partial oxidation has taken place, which has, of course, resulted in an increase of weight.

GRAVIMETRIC DETERMINATION OF ZINC.

Zinc may be determined gravimetrically by precipitation as zinc sulphide as follows: To a measured portion of the solution, free from all metals (except zinc) of Groups I, II, III, and IV, add ammonium chloride, ammonium hydroxide, and ammonium sulphide, as in qualitative analysis. Filter the precipitated zinc sulphide on to counterpoised filters, wash thoroughly with water containing a little ammonium sulphide, dry in an atmosphere free from oxygen (hydrogen or hydrogen sulphide), and weigh as zinc sulphide.

GRAVIMETRIC ASSAY OF GOLD AND SILVER IN THE DRY WAY.

It is often more convenient to determine gold and silver by the fire assay than by the volumetric methods previously given. This is accomplished usually by fusion with an excess of lead and a borax flux. The mixture is kept at a high heat for upwards of thirty minutes, with a current of air passing over the surface of the molten metals. This serves to oxidize and carry away the baser metals, leaving the gold and silver with but a slight amount of lead, possibly a trace of copper and tin. The purification is completed by cupellation. When the traces of lead and other metals are absorbed by the cupel or are driven off as volatile oxides, the button of gold and silver is next cooled *very slowly* and carefully weighed. From this the silver may be dissolved by nitric acid unless the gold is in considerable excess,

which would rarely be the case. If it happens that the gold is present in sufficient quantity to prevent the solution of the silver in nitric acid a known weight of pure silver may be added in amount sufficient to increase the percentage of silver to seventy-five or over, fused, and then all the silver dissolved out with nitric acid, leaving the gold.

The gold which has resisted solution may be found as small black particles or grains in the bottom of the crucible. This should be carefully washed with distilled water by decantation, very carefully dried and brought to a red heat, which will give a button of pure gold. This may be weighed and the weight subtracted from the weight of gold and silver button previously obtained.

QUANTITATIVE ANALYSIS OF DENTAL ALLOYS CONTAINING Au, Sn, Ag, Cu, Zn.

Weigh accurately 0.5 gram of alloy which has been reduced to fine filings and from which all particles of iron have been carefully removed by a magnet, transfer to a beaker, and dissolve in 15 c.c. of strong HNO_3 and 10 c.c. of H_2O by aid of gentle heat. If the sample contains tin or gold, complete solution will not be effected, but, by watching the character of the sediment through the bottom of the beaker, it is possible easily to determine when the alloy has been completely disintegrated.

If silver is to be determined by titration with NaCl and K_2CrO_4, evaporate on a water-bath till all nitric acid has been expelled.

If silver is to be determined by the sulphocyanate solution, evaporation at this point is not necessary. In either case, make the whole solution up to 250 c.c. with distilled water; then filter out tin and gold, following the method given under gravimetric determination of tin (page 163), reserving the filtrate before any wash-water has been added. For convenience this filtrate may be marked " A." Titrate this filtrate (" A ") for silver as follows:

Take a measured volume, about 30 c.c., and place in a porcelain dish with ferric alum as indicator.

Then place the standard KCyS in the burette and titrate till the faint red color is produced.

Suppose 8 c.c. of KCyS is used. The weight of silver in 1 c.c. of a decinormal solution is 0.0108 gram. Multiplying 8 by 0.0108 = 0.0864. Divide by number of c.c. of solution taken, 0.0864 ÷ 30 = 0.00288 gram Ag in 1 c.c. of solution.

Multiply by whole number of cubic centimeters and divide by weight of alloy taken and result will be percentage of silver.

Take 100 c.c. of filtrate " A " and precipitate silver by slight excess of HCl. Filter and wash precipitate thoroughly with warm water. Concentrate filtrate and wash-water, which may be designated as filtrate " B." Pass H_2S gas into " B " till copper is entirely separated as CuS. Filter and wash CuS seven or eight times with dilute H_2S water. Reserve filtrate and wash-water as filtrate " C." Dissolve CuS in dilute HNO_3, wash paper carefully, concentrate, and determine amount of copper by deposition upon platinum (page 164). Concentrate filtrate " C " and determine zinc by volumetric method given on page 162. Gold and tin in residue insoluble in nitric acid may be determined by method given on pages 163 and 158.

QUESTIONS IN VOLUMETRIC WORK.

Why is an N/10 solution of hydrochloric acid more generally serviceable than a similar solution of oxalic acid?

Why use nitric acid for titration of chlorine in urine by use of KCNS?

PART IV.

MICROCHEMICAL ANALYSIS.

CHAPTER XVIII.

METHODS.

THE advantages of microchemistry are many, as claimed by its enthusiastic advocates, and there are two particulars in which these methods strongly recommend themselves to the dental practitioner: (1) Microchemical analysis deals with exceedingly minute portions of matter, making the examination of very small particles of substance easily possible. (2) Three or four one-ounce " drop-bottles " and a few two-drachm vials will contain all necessary reagents, and in consequence three feet of bench-room will furnish ample laboratory space.

The principles of microchemical analysis are, of course, the same as for any analysis, but the processes employed are quite different and need some explanation. In microchemical analysis the production of crystals of characteristic form furnishes perhaps the most rapid method of detection of an unknown substance, and in this we are greatly aided by the use of polarized light, which not only helps in the differentiation of crystals but often makes it possible to see and distinguish small or transparent crystals which might otherwise escape notice altogether.

Use of Microscope. — For the examination of the crystals mentioned in this chapter, also for the work required on saliva or urine, lenses of comparatively low power are sufficient. For most of the microchemical tests, a No. 3 Leitz or a 16-mm. Bausch & Lomb objective will be found satisfactory. For a few micro-

chemical tests and for urine, an 8-mm. Bausch & Lomb or a
No. 5 Leitz objective will give better results in the hands of a
beginner than one of higher power.

In using the microscope for microchemistry, the preparation
should *always* be covered with a cover glass and the examination
be made with the low-power lens if possible. The object in
covering is to prevent any action by reagent upon the objective.
As a further precaution, it is well to form the habit of first
lowering the objective and then focusing by upward movement
of the draw-tube.

Formation of crystals may be brought about in two ways:
first, by precipitating insoluble crystalline salts by use of re-
agents, as in ordinary qualitative analysis; *second*, by allowing
salts to crystallize by spontaneous evaporation of the solvent.

If the first method is to be employed it is essential to have
the dilution fairly constant in order to obtain crystals which shall
be comparable with those obtained at other times or by other
individuals. The tendency of strong solutions is to give amor-
phous precipitates. Sometimes the precipitate will be amor-
phous when first thrown down, but upon standing will assume
crystalline form. To secure the uniformity of results necessary
to correct deductions, the following method of procedure should
be *exactly* followed *every* time.

The reagent should be of uniform strength, usually one or
two per cent. Place on a clean microscope-slide a small drop of
the solution to be tested, and as close as possible without touching
it, one of about equal size of the reagent to be used. Now bring
the drops together by tapping the slide or with a small glass rod.
If a precipitate forms immediately, *cover with a cover-glass* (this
must *always* be done) and examine with the microscope. If the
precipitate is crystalline, note the form, and in any case, whether
crystalline or not, repeat the test after diluting the unknown
solution one-half. If the second test gives an amorphous pre-
cipitate, or crystals of different shape from the first, *continue*

the *dilution* of the *unknown* till a point is reached when admixture with the drop of reagent gives *no immediate* precipitate, but one appearing in a few seconds' time (five to thirty). In this way we have produced the precipitate under standard conditions or as nearly such as is possible with unknown solutions.

Until thoroughly familiar with the forms obtained by drying the various reagents, it is well to evaporate a small drop of the reagent alone, on the same slide on which a test is made, for the sake of subsequent comparisons.

Filtration in microchemical examinations, when perhaps only a few drops of solution are to be had, may be effected in a very satisfactory manner and without appreciable loss by absorption as follows:

Cut a filter-paper about 1 cm. wide and 6 cm. long, double it and crease the middle so that it assumes the shape of an inverted V. Put the solution to be filtered in a small watch-glass placed at a slight elevation above a microscope slide; now place one " leg " of the strip of filter-paper in the watch-glass, allowing the end of the other to touch the slide. By capillary attraction the clear solution will follow over the bend in the strip of paper and a drop or two of perfectly clear filtrate suitable for the test will be found upon the slide.

Evaporation of a *solution* is best effected on a small watch-glass *held in the fingers* and moved back and forth over a low Bunsen flame, or else placed over a water-bath.

The purpose of the microchemical tests here outlined is not so much a method of general qualitative analysis, to which they are not suited, as it is a specific application of well-known reactions to concrete examination of substances, the uses and probable composition of which are known. The details of the various tests will be given under classification furnished by the substances investigated.

Our study may include alloys and amalgams, teeth, tartar, dental anesthetics, cement, mouth-washes, antiseptics, disin-

PLATE II. — MICROCHEMICAL ANALYSIS.
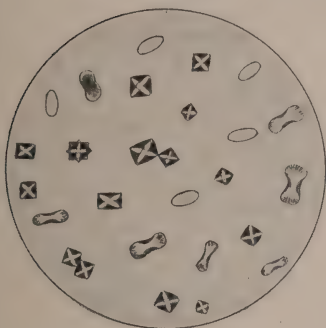
FIG. 1.
Calcium Oxalate.

FIG. 2.
Cadmium Oxalate.

FIG. 3.
Strontium Oxalate.

FIG. 4.
Sodium Oxalate (P.L.).
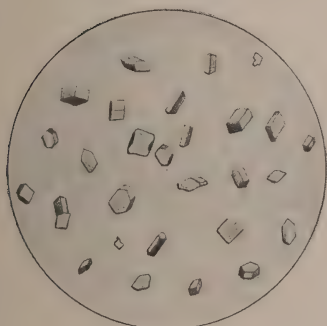
FIG. 5.
Oxalate of Urea.
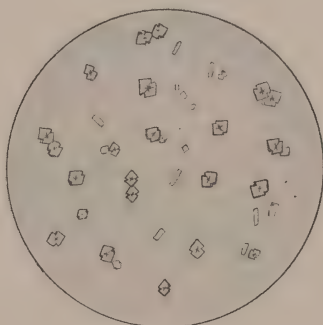
FIG. 6.
Zinc Oxalate.

PLATE III.—MICROCHEMICAL ANALYSIS.
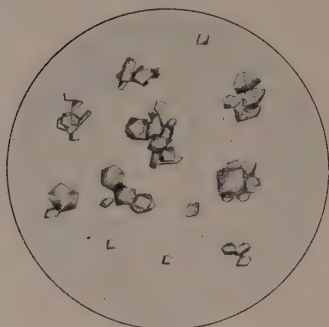
FIG. 1.
Ammonium Platinic Chloride.
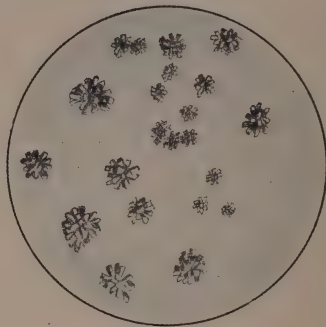
FIG. 2.
β Eucaine and Platinic Chloride.
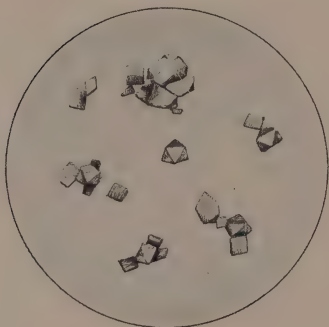
FIG. 3.
Potassium Platinic Chloride.
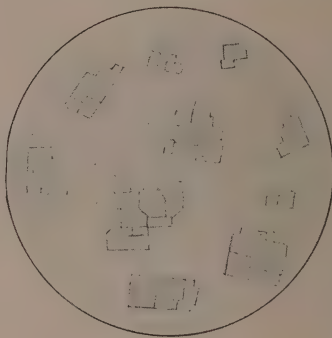
FIG. 4.
Cocaine and Potassium Permanganate.
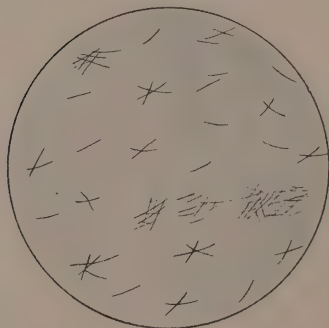
FIG. 5.
Tri-brom-phenol.
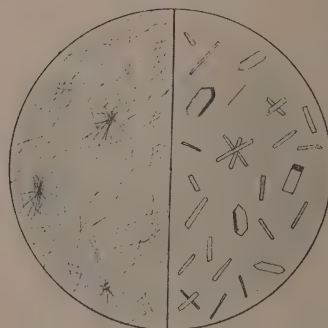
FIG. 6.
Morphine.

fectants, and sediments obtained from the saliva and from the urine.

The following crystals are selected as among those most frequently met with in the analysis of the above substances or best suited for the study of microchemical processes, and the student should make each test here indicated and carefully draw the crystals produced:

1. Calcium oxalate from 2% $H_2C_2O_4$ and $CaCl_2$ solutions (Plate II, Fig. 1).

2. Cadmium oxalate from 2% $H_2C_2O_4$ and $CdSO_4$ solutions (Plate II, Fig. 2).

3. Strontium oxalate from 2% $H_2C_2O_4$ and $Sr(NO_3)_2$ solutions (Plate II, Fig. 3).

4. Sodium oxalate by evaporation of aqueous solution, also by evaporation of urine containing $Na_2C_2O_4$ (polarized light) (Plate II, Fig. 4).

5. Urea oxalate from 2% $H_2C_2O_4$ and urea solution (Plate II, Fig. 5).

6. Ammonium-magnesium-phosphate from magnesium mixture * and sodium phosphate (Plate IV, Fig. 2).

7. Ammonium platinic chloride (Plate III, Fig. 1). For preparation of crystals see pages 46 and 47.

8. Potassium platinic chloride, H_2PtCl_6 (Plate III, Fig. 3). For preparation of crystals see page 47.

9. Sodium urate by evaporation (polarized light) (Plate X, Fig. 3, opp. page 255).

10. Crystals formed from cocaine and potassium permanganate (Plate III, Fig. 4).

11. Crystals formed from phenol and dilute bromine water (tribromphenol) (Plate III, Fig. 5).

12. Crystals formed from morphine solutions and ammonia (morphia) (Plate III, Fig. 6).

* Magnesium mixture as used in urine analysis to precipitate phosphates contains $MgCl_2$ (or $MgSO_4$), NH_4Cl, and NH_4OH.

13. Crystals formed from morphine and Marme's reagent (Plate IV, Fig. 1).

14. Platinum chloride and β-eucaine (Plate III, Fig. 2).

15. Stovaine and platinum chloride (Plate IV, Fig. 4.).

16. Alypin and KI (Plate IV, Fig. 6).

The list may be extended to include the crystals produced by various alkaloidal salts with the common reagents, also substances usually employed in the manufacture of the various dental preparations.

PLATE IV.—MICROCHEMICAL ANALYSIS.
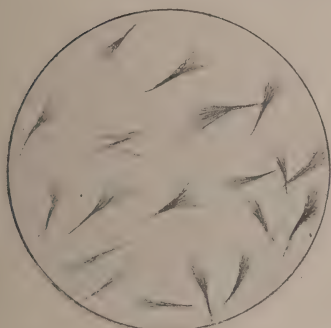
FIG. 1.
Morphine and Marme's Reagent.

FIG. 2.
Magnesium Ammonium Phosphate.

FIG. 3.
Cocain with Tin Chloride.
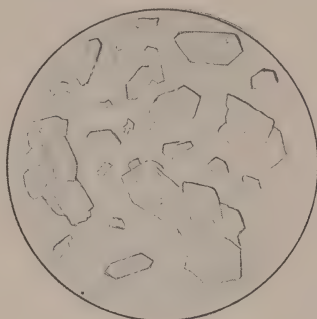
FIG. 4.
Stovaine and Platinic Chloride.
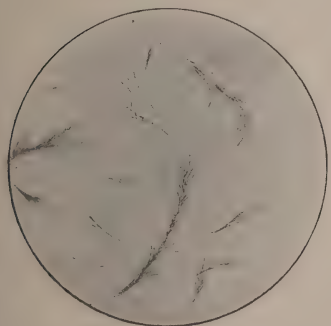
FIG. 5.
Palmitic Acid.
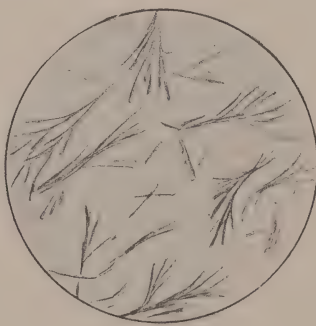
FIG. 6.
Alypin and Potassium Iodide.
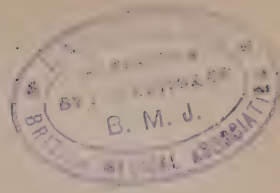
CHAPTER XIX.

LOCAL ANESTHETICS AND ANTISEPTICS.

(Also some other substances commonly used in dental preparations.)

In considering the chemistry of local anesthetics we may divide them into two classes as follows:

First, those of definite or well-known composition, and

Second, preparations of a proprietary nature, the composition of which is always problematical.

In the first class will be found cocaine, eucaine, tropacocaine, acoin, ethyl chloride, etc., which will be later alphabetically considered. The second class contains a large number of preparations of all degrees of value, among them some of exceeding merit and largely used, others of doubtful worth, some worthless if not dangerous. Many of the preparations of this class contain cocaine as the anesthetic, and frequently a little nitroglycerin as a cardiac stimulant to counteract the depressant effect of the alkaloid. Carbolic acid and oil of cloves are also frequently used.

Many of the constituents of this class of anesthetics may readily be identified by the processes of microchemical analysis to which previous reference has been made; others may be detected by special tests, some of which are given under the various substances in the following list. This list has been extended to include a considerable number of preparations of common occurrence.

Acoin, a synthetic compound, chemically diparanisyl-monophenetyl-guanidine hydrochloride $\left(C \left\langle \begin{array}{c} (NC_6H_4OCH_3)_2 \\ (NC_6H_4OC_2H_5) \end{array} \right. HCl \right)$

173
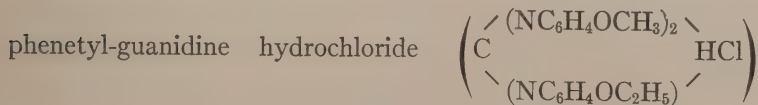
soluble in both alcohol and water. Strongly antiseptic and a valuable anesthetic, especially in conjunction with cocaine. Acoin should be used only in solution and this should be kept in a dark place.

Adrenalin, a valuable hemostatic and frequently used in conjunction with dental anesthetics, is the active principle of the suprarenal gland or capsule. It occurs as very small white crystals which are not very stable and only slightly soluble in water, hence the article is usually sold in solution with sodium chloride, according to the following formula taken from a commercial sample:

Adrenalin chloride, 1 part; normal sodium chloride solution (with 0.5% chloretone), 1000 parts. This solution is usually diluted with the normal (0.6%) salt solution. According to the Druggists' Circular, preparations similar to the above are also marketed under the names of adrenol, adnephrin, hemostatin, suprarenalin (Armour & Co.), suprarenin, etc., see Epinephrine.

Alypin. — Benzoyl - dimethylamino - methyl-dimethylamino-butane hydrochloride, white crystalline, hygroscopic, melts at 169° C. Soluble in water and alcohol.

Alypin can be sterilized without decomposition, is not half so poisonous as cocaine and is cheaper. Is used in 2% solution. Solution should be freshly made and prolonged boiling avoided. Sometimes used with adrenalin. (Cosmos, 1908, p. 889.)

Alypin nitrate occurs as a white, crystalline powder melting at 159° C., readily soluble in ether. Mfrs.: Farbenfabriken of Elberfeld, Elberfeld (Germany) and New York. (Mod. Mat. Med., page 21.)

Test. — Alypin gives needle-shaped crystals with potassium iodide, easily produced. (Plate IV, Fig. 6.)

Ammonium Bifluoride is strongly recommended as a solvent for tartar by Dr. Joseph Head of Philadelphia. In Items of Interest, Vol. 31, page 174, Dr. Head gives the following method for its preparation. Hydrofluoric acid is neutralized with am-

monium carbonate, the solution filtered and evaporated to half its bulk, the original volume restored by adding more hydrofluoric acid and then the resulting mixture is again concentrated to half its volume by evaporation.

Anesthol, or Anæsthol, is a mixture of ethyl chloride and methyl chloride, used as a local dental anesthetic. The name is also applied to a general anesthetic given by inhalation and consisting of a mixture of ethyl chloride 17 parts, chloroform 35.89 parts, and ether 47.1 parts.

Anæstheaine, a local anesthetic, contains five grains of stovaine to the fluid ounce.

Argyrol, a protein compound of silver, occurs as dark brown crystals containing 30% of silver. It is easily soluble in water. It does not precipitate chlorine nor coagulate albumin, and is recommended for use in place of ordinary silver nitrate.

Aristol is given by the U. S. D. as a synonym for dithymoldiiodide which contains 45% of iodine and is used as an antiseptic similarly to iodoform.

Atropine, an alkaloid obtained from belladonna, usually used combined with sulphuric acid, $(C_{17}H_{23}NO_3)_2H_2SO_4$; the alkaloid is only sparingly soluble in water but the sulphate is easily soluble, dissolving in about one-half part of water at ordinary temperature. A one per cent. solution is said to produce complete insensibility of the nerves in cases in which an artificial tooth is inserted in a living root. (U. S. D., page 249.)

Tests. — Atropine may be separated from a local anesthetic by first rendering the mixture alkaline with ammonia and shaking with chloroform. Upon evaporation of the chloroform solution on a watch-glass the resulting residue may be tested by adding a drop or two of sulphuric acid and a trace of potassium bichromate and a little water. The odor of bitter almonds is produced. A more conclusive test is to convert the alkaloid, which has been dissolved by the chloroform, into a salt by the addition of a few drops of acetic acid, evaporating to *complete* dryness, taking

up in a few drops of distilled water and placing one or two drops of this solution in the eye of a cat, when, if atropine is present, a dilation of the pupil occurs in from fifteen minutes to an hour and a half, according to amount present.

Borax. — Sodium tetraborate, $Na_2B_4O_7$, is used in antiseptic solutions and may be detected as follows: evaporate a little of the solution to dryness, add a little HCl, evaporate to dryness a second time, then add a very dilute HCl solution containing tincture turmeric. Upon drying this mixture a beautiful pink color appears. If much organic matter is present it may be burned off in the Bunsen flame *before* the addition of any acid.

Carbolic Acid. — See Phenol.

Chloral Hydrate, $CCl_3CHO.H_2O$, a crystalline solid composed of trichloraldehyde, or chloral, with one molecule of water (U. S. P.), easily soluble in water, may become with alcohol a chloral alcoholate comparatively insoluble in water.

Tests. — Chloral may be detected by adding to the suspected mixture a few cubic centimeters of fairly strong alcoholic solution of KOH or NaOH with one drop of aniline oil and heating, when isobenzonitril is produced, which has a peculiarly disagreeable and characteristic odor. This test is also given by chloroform, which is produced by heating chloral hydrate with caustic alkali. If more than traces of chloral are present this latter reaction may be a sufficient test.

Chloretone, $CCl_3COH(CH_3)_2$, is the commercial name of acetone-chloroform or tertiary trichlorbutyl alcohol. Made from chloroform, acetone, and an alkali, and occurs as small white crystals, with taste and odor like camphor. It is dissolved by alcohol and glycerol and to a slight extent by water.

Chloroform, trichlormethane, $CHCl_3$, prepared by action of chlorinated lime on acetone. Chloroform is a heavy colorless liquid with a specific gravity of 1.490 at 15° C. Is very volatile and used as a solvent for gutta-percha, caoutchouc, many

vegetable balsams, camphor, iodine, bromine, and chlorine; it also dissolves sulphur and phosphorus to a limited extent.

Tests. — It may be detected by its odor, when heated, or by the isobenzonitril test to which reference has been made under chloral hydrate.

Cocaine is the alkaloid obtained from erythroxylon coca. The hydrochlorate, $C_{17}H_{21}NO_4HCl$, is the salt most usually employed. This is easily soluble in water and very largely used as a dental anesthetic in a one or two per cent. solution.

Tests. — Cocaine solutions respond to the usual alkaloidal reagents. With 1% solution potassium permanganate gives pink plates resembling cholesterol (Plate III, Fig. 4) in form but not in color.

Dilute cocaine solution with picric acid gives a yellow precipitate which becomes crystalline on standing. Quite characteristic crystals may also be obtained from dilute cocaine solutions and stannous chloride in the presence of free HCl.

Creosote. — A mixture of phenols derived from the destructive distillation of wood tar. It is a heavy oily liquid acting when pure as an escharotic. It is analogous in many respects to carbolic acid and may be used for similar purposes. To distinguish between creosote and carbolic acid, boil with nitric acid until red fumes are no longer given off. Carbolic acid will give yellow crystalline deposit; creosote will not. An alcoholic solution of creosote is colored emerald green by an alcoholic solution of ferric chloride. Phenol is colored blue.

Cresol is the next higher homologue to phenol, having a formula $C_6H_4CH_3OH$, boiling at $198°$ C. It is largely used, usually together with allied compounds from coal-tar, as antiseptic and disinfectant solutions.

Ektogan. — Peroxide of zinc, ZnO_2, designed for external use.

Epinephrine. — The active principle is the suprarenal glands. Chemically it is an *o*-dihydroxyphenyl-ethanolmethyl-

amine, $C_6H_3(OH)_2.CHOH.CH_2NHCH_3$. This is a weak base which combines with hydrochloric acid to form the hydrochloride in which form it is usually used in dilutions of one part to a thousand. It acts as a cardiac stimulant causing rise in blood pressure with slower heart action, acting somewhat in the same way as digitalis.

Ethyl Chloride, monochlorethane, C_2H_5Cl. This is a gaseous substance at ordinary temperature, but when used as a dental anesthetic it is compressed to a colorless liquid which has a specific gravity of 0.918 at 8° C., is highly inflammable and usually sold in sealed glass tubes of from ten to thirty grams each.

β-Eucaine is the hydrochlorate of bezoylvinyldiacetone-alkamine, and occurs as a white, neutral powder, soluble in about thirty parts of cold water. It is used like cocaine as a local anesthetic, and is claimed to be less toxic, and sterilizable by boiling without danger of decomposition. It is usually applied in from one to five per cent. solutions, which are conveniently prepared in a test-tube with boiling water. It is also marketed in the form of $1\frac{1}{2}$ and 5-grain tablets. (Druggists' Circular.)

Test. — β-Eucaine gives characteristic crystals with platinic chloride. (Plate III, Fig. 2.)

Eucain Lactate. — " Eucain lactate is used in two to five per cent. solution as a local anesthetic in ophthalmic and dental practice and in ten to fifteen per cent. solution when used in the nose or ear." (Review of American Chemical Research, page 97, 1905.)

Eudrenin is a local anesthetic marketed in capsules of 0.5 c.c. containing 1/12 grain of eucain and 1/4000 grain of adrenalin hydrochloride. It is used as a local anesthetic, chiefly in dentistry. The contents of one or two capsules, according to the number of teeth to be extracted, are injected into the gums ten minutes before extraction. Mfrs.: Parke, Davis & Co., Detroit, Mich. (Mod. Mat. Med., page 147.)

Eugenol, $C_{10}H_{12}O_2$, synthetical oil of cloves. Eugenol is miscible with alcohol in all proportions. Exposure to air thickens and darkens it. Should be kept in well-stoppered amber-colored bottles (U. S. D.).

Europhen — recommended by Dr. J. P. Buckley as a substitute for iodoform (Dental Review, Vol. 21, page 1284).

Di-iso-butyl-cresol is described as a bulky yellow powder of faint saffron odor and containing 28% of iodine. (Mod. Mat. Med., page 152.)

Formaline, Formol, Formine, etc., are commercial names for a 40% aqueous solution of formaldehyde, HCHO, prepared by the partial oxidation of methyl alcohol. Formaline is a powerful disinfectant very generally used. (For test see page 386, Exp. 83.)

Glycerol is a triatomic alcohol, $C_3H_5(OH)_3$, a colorless liquid of syrupy consistence and sweetish taste, specific gravity 1.250 at 15° C. It is easily soluble in either water or alcohol.

Tests. — Upon heating with acid potassium sulphate (solid) it is decomposed, giving off odor of acrolein, which is usually sufficient for its identification. A further test may be made by moistening a borax bead on a platinum wire with the suspected solution (after concentration) and holding in a non-luminous flame, to which it will give a deep-green color which does not persist. Glycerol when present is apt to interfere with characteristic crystallization of many precipitates.

Gram's Solution, Kuhne's modification, contains two grams of iodine, and four grams potassium iodide in 100 c.c. of water.

Gutta-percha. — The name signifies scraps of gum. It is obtained as a milky exudate from a number of tropical trees. It is soluble in ether, chloroform, carbon disulphide, toluene, and petroleum ether. It may be freed from impurities by shaking the solution with calcium sulphate, which will mechanically carry coloring matter and other impurities with it as it slowly settles out from the mixture. It is not soluble in alcohol or in water.

Heroin is a diacetic ester of morphine. It is usually obtained as the hydrochloride and occurs as a white powder, soluble in two parts of water. Its action is similar to that of morphine; it answers to the usual color tests for morphine, but may be distinguished from it by the fact that it will yield acetic ether upon heating with alcohol and sulphuric acid.

Hopogan (also known as biogen) is a peroxide of magnesium, MgO_2, recommended as a non-poisonous and non-astringent intestinal germicide.

Hydrogen Peroxide, or dioxide, H_2O_2, is, when pure, a syrupy liquid without odor or color. It is sold under various trade names in aqueous solution containing about 3% and yielding upon decomposition about 10 volumes of oxygen gas. It is used also as an escharotic in etherial solutions containing twenty-five to fifty per cent. H_2O_2. Peroxide solutions may be concentrated by heat without decomposition if kept *perfectly* free from dirt or traces of organic matter. It is readily prepared by treatment of metallic peroxides, as BaO_2 with dilute acids.

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$
or
$$BaO_2 + H_2O + CO_2 = BaCO_3 + H_2O_2.$$
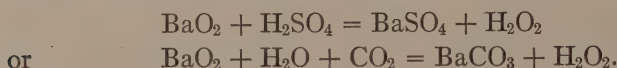
This latter reaction has the advantage of producing an insoluble barium compound and at the same time introducing no objectionable acid. The peroxides of sodium, calcium, magnesium, and zinc may also be used; ZnO_2, however, is comparatively expensive and used in powder form as an antiseptic dressing rather than as a source of H_2O_2. Na_2O_2 is valuable as a bleaching agent, because for this purpose an alkaline solution is required and the solution of Na_2O_2 in water produces both alkali and H_2O_2 according to the following reaction:

$$Na_2O_2 + 2 H_2O = 2 NaOH + H_2O_2.$$
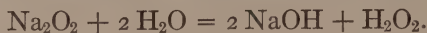
Sodium perborate (page 185), also sold as euzone, is a powder which will produce H_2O_2 in water. Commercial H_2O_2 solutions

are usually acid in reaction, as such solutions are more stable than if neutral or alkaline.

Test. — Add to a solution of H_2O_2 a few drops of bichromate of potassium solution and a little dilute H_2SO_4. Shake cold with a little ether in a test-tube. The ether should be colored blue. (For further tests see experiments.)

Lugol's Caustic Iodine is made of iodine and potassium iodide, one part of each dissolved in two parts of water.

Lugol's Iodine Solution. — See appendix under Iodine Solution.

Menthol is the stearopten obtained from the oil of peppermint. It is a volatile crystalline substance having a formula $C_6H_9OHCH_3C_3H_7$. Menthol is but slightly soluble in water but freely soluble in alcohol, ether, chloroform, or glacial acetic acid. The presence of menthol may usually be detected by its odor. If the odor should be suggestive but not distinctive it is well to place a little of the substance on a filter-paper, rub it between the thumb and finger, thereby obtaining a " fractional evaporation," when the more easily volatile substance will pass off first, thus producing a partial separation of substances.

Mercuric Chloride, corrosive sublimate, $HgCl_2$, is soluble in about sixteen parts of water and three parts of alcohol. It is a powerful antiseptic, in aqueous solution 1/1000 to 1/5000, but should never be used in mouth-washes.

Tests. — A drop of the suspected solution with a trace of potassium iodide will give a red precipitate of mercuric iodide soluble in excess of either reagent. With lime-water or fixed alkaline hydroxides a black precipitate is produced. A drop of mercurial solution placed on a bright copper plate will leave a tarnished spot due to the reduction of the mercuric salt and subsequent amalgamation of the metal.

Methethyl. — Ethyl chloride mixed with a little methyl chloride and chloroform is said to be the composition of a local anesthetic sold under the name of methethyl (U. S. D.).

Methyl Chloride, CH_3Cl, is a colorless gas which condenses to a liquid at $23°$ C. Methyl chloride is easily soluble in alcohol, somewhat in water, and is used in a similar manner to ethyl chloride.

Morphine, $C_{17}H_{19}NO_3$, alkaloid from opium. Solutions for use are made from the sulphate, hydrochlorate, or acetate. The alkaloid itself is insoluble in water; its salts are easily soluble.

Morphine may be separated from solutions containing it by making the solution alkaline with ammonia, and shaking out the precipitated alkaloid with warm ethyl acetate. Upon evaporation of the solvent the residue may be tested with Fröhde's reagent (sodium molybdate, 1%, in strong sulphuric acid). The color obtained should be a *violet*, changing usually to brown; a pure blue color is not distinctive for morphine. If the morphine solution is of sufficient strength the addition of ammonia will produce minute crystals of the alkaloid as shown on Plate III, Fig. 6. Dental anesthetics containing morphine will give precipitates with the usual alkaloidal reagents. Marme's reagent (CdI_2) gives crystals represented on Plate IV, Fig. 1.

Nirvanin, hydrochloride of diethyl-glycocoll-*p*-amino-*o*-oxy-benzoic-methylester, of the formula

$$(CH_2N) = (C_2H_5)_2HCl$$
$$|$$
$$CO.NH.C_6H_3(OH)COOCH_3.$$
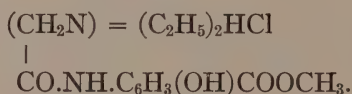
White prisms soluble in water and in alcohol, melt at $185°$ C., violet reaction with ferric chloride.

Nitroglycerin, $C_3H_5(NO_3)_3$, is used as a cardiac stimulant in alcoholic solution, the U. S. P. Spiritus Glonoini, containing 1% by weight of the substance.

Test. — Extract the dry substance, or the evaporated residue, with alcohol. Filter and evaporate to dryness. Add 1 c.c. of sulphuric acid and 1 c.c. of phenoldisulphonic acid. Heat over a water bath for five minutes; add water and excess of ammonia.

A deep yellow color of ammonium picrate indicates nitrates in the original substance. Exp. No. 148, p. 397.

Novocaine, discovered by Uhlfelder and Einhorn, is a hydrochloride *p*-aminobenzoyl-diethylamino-ethanol. It occurs as thin colorless needles; melts at 156° C., soluble in one part water and thirty parts alcohol. It is seven times less toxic than cocaine, and three times less toxic than stovaine. It can be sterilized by boiling, and is used in 1/2 to 2% solution often with adrenalin 1/1000. (Mod. Mat. Med., page 275.)

Novocaine, if intended to represent a solution which is isotonic with the blood corpuscles, must be dissolved in a 0.92 per cent. sodium chloride solution. (Dental Cosmos, 1910, page 605.)

Oil of Cloves, oil of Gaultheria, and other essential oils may be detected by the same process of fractional evaporation as suggested for menthol. In testing for the presence of any substance by its odor, it is usually necessary to make a comparative test on known samples using the same methods.

Orthoform, $C_6H_3OH(NH_2)COOCH_3$, methylpara-amino-meta-oxybenzoate, used as an anesthetic and antiseptic, is without odor, color, or taste, is slightly soluble in water, and easily soluble in alcohol or ether.

Phenol. — Carbolic acid, C_6H_5OH, obtained from the destructive distillation of coal-tar. A light oily liquid of specific gravity of 0.94–0.99. Carbolic acid is usually obtained as a white crystalline mass soluble in twenty parts of water. The pure acid turns pink with age, but does not suffer deterioration on account of this change of color. The addition of from five to eight per cent. of water will cause liquefaction of the crystals and the preparation becomes permanently liquid. It is easily soluble in glycerol and strong solutions may thus be prepared. Carbolic acid is sometimes added to local anesthetics with the intent of rendering the solution sterile, but as shown by Dr. Endelman (Dental Cosmos, Vol. 45, page 44) it would be neces-

sary, in order to prevent the development of micro-organisms, to add the acid in proportion that would render the solution unfit for hypodermic purposes.

Tests. — Phenol may be detected in the majority of preparations by the addition of bromine-water, which gives white crystals of tribromphenol (see Plate III, Fig. 5). See also Exp. 145.

Phenol Compound. — Dr. Buckley's formula for treatment of root canals — menthol 1.3 grams, thymol 2.6 grams, and phenol 12 c.c.

Potassium Hydroxide, KOH, gives an alkaline reaction to litmus paper and may be detected by the ordinary methods of inorganic analysis.

Rhigolene is a light inflammable liquid obtained from petroleum, boiling at about 18° C., used as a spray for the production of low temperature, similarly to methyl or ethyl chloride. It is readily inflammable and the vapor, mixed with certain proportions of air, is explosive. It should be kept in a cool place.

Ringer's Solution, which is used as a solvent for Novocaine and other anesthetics has the formula:

Sodium Chloride 0.50
Calcium Chloride 0.04
Potassium Chloride. 0.02
Distilled water 100.00

Saccharin. — Saccharin is official in the ninth revision of the Pharmacopœia as benzosulphinidum. It is a derivative of toluene having a formula of $C_6H_4COSO_2NH$, being benzoyl-sulphonimide. It is a white crystalline powder melting at 219° to 222° C.

It is said to be at least three hundred times sweeter than cane sugar and is used in mouth-washes, tooth-paste, etc., as a flavor and an antiseptic.

Test. — Add a few drops of potassium hydroxide solution to a little saccharin; heat for a few minutes. Acidify with

hydrochloric acid; add a few drops of ferric chloride; when a reddish brown or purplish color is produced.

Silver Nitrate, $AgNO_3$, crystallizes in colorless plates without water of crystallization; used as an antiseptic, disinfectant, or escharotic. It is freely soluble in water and may be detected by the ordinary methods of qualitative analysis (page 20).

Sodium Chloride, NaCl, is a constituent of many preparations designed to be used hypodermically. Experience has proved the value of such addition; perhaps the reason for its desirability is given by Dr. G. Mahe, of Paris, in the Dental Cosmos for September, 1903, in the statement that sodium chloride added in excess to a toxic substance diminishes its toxicity by one-half, and this has been demonstrated particularly with cocaine.

Sodium Perborate, a powder having the composition $NaBO_3.4 H_2O$, which will furnish 10% of available oxygen and produce H_2O_2 with water; very stable and recommended as a bleach-powder.

Sodium perborate may be made by thoroughly mixing sodium peroxide (Na_2O_2) with crystallized boric acid and stirring the mixture gradually into cold water. The proportions recommended by V. E. Miegeville in the Dental Cosmos for 1905, page 1381, are 78 grams of the sodium peroxide, 248 grams of the boric acid, and two liters of water. The sodium perborate is formed spontaneously and separates from the solution as a white crystalline powder. Its solubility is increased by addition of weak organic acids, citric or tartaric.

Sodium Peroxide, Na_2O_2. — A white powder easily soluble in water, usually with evolution of more or less oxygen and formation of hydrogen dioxide.

Somnoform. — A general anesthetic administered in manner similar to chloroform; introduced by Dr. Rolland, of Bordeaux; consists of 60% ethyl chloride, 35% ethyl bromide, and 5% methyl bromide. (Dental Cosmos, Vol. XLVII, page 236.)

Stovaine. — Benzoylethyldimethyl-aminopropanol hydrochloride, $C_{14}H_{21}O_2N.HCl$, closely related to alypin, small shining scales freely soluble in alcohol or water. Incompatible with alkalies and all alkaloidal reagents. Can be sterilized by boiling. (Mod. Mat. Med., 2nd edition.)

It melts at 175° C., is very soluble in water, and gives reaction similar to cocaine, which is also a benzoyl derivative. (U. S. D., page 1661.)

It is less powerful than cocaine and physiologically incompatible with adrenalin. (Dental Cosmos, 1905, page 146.)

Test. — Stovaine gives rather irregular but characteristic crystals with platinic chloride. (Plate IV, Fig. 4.)

Suprarenal Glands. — The official preparation consists of dried glands obtained only from animals used for food by man, and which must contain not less than 0.4% nor more than 0.6% of epinephrine.

Tannic Acid, or tannin, sometimes called gallotannic acid, is an astringent organic acid obtained from nutgalls. It may be obtained as crystals carrying two molecules of water, $HC_{14}H_9O_9.2 H_2O$. Tannic acid is a white or slightly yellowish powder soluble in about one part of water or 0.6 part alcohol. It is used as an alkaloidal precipitate, also in astringent washes. It may be detected by the addition of ferric solutions which form with it a black tannate of iron of the nature of ink.

Thymol, $C_6H_3(CH_3)(OH)(C_3H_7)$ 1 : 3 : 4. This is a phenol which occurs in volatile oils of thymus vulgaris (Linne). Melts at 44° C.; sparingly soluble in water, easily in alcohol and ether.

Tests. — It may usually be detected by its odor or by dissolving a small crystal in 1 c.c. of glacial acetic acid, when, if six drops of sulphuric acid and one drop of nitric acid be added, the liquid will assume a deep bluish-green color. (U. S. D.)

Thymol iodide, diiododithymol, $(C_6H_2.CH_3.C_3H_7OI)_2$, a valuable antiseptic containing forty three per cent. of iodine. It is

brown powder insoluble in water, slightly soluble in alcohol, easily soluble in chloroform or ether.

Thymophen, a mixture of equal parts of thymol and phenol.

Thyroids. — The dried, powdered, thyroid glands of animals used for food by man, freed from connective tissue and fat, containing not less than 0.17% or more than 0.23% of iodine, constitutes the official preparation used as a remedy in myxedema and other cases of perverted metabolism.

Trichloracetic Acid occurs as deliquescent crystals, readily soluble in water. Distils at 195° C. and is a powerful caustic. Dilute solutions are recommended for treatment of pyorrhea.

Tropa-cocaine is an alkaloid originally isolated by Giesel from the leaves of the small-leaved coca-plant of Java and introduced by Arthur P. Chadbourne, Harvard Medical School. Used hypodermically in normal salt solution. It is probably superior to cocaine, but rather more expensive. It is obtained as an oil which, when quite dry, solidifies in radiating crystals, melting at 49° C. It is easily soluble in alcohol.

A number of commercial mouth-washes and local anesthetics will be given to the class for identification, the object being to familiarize the student with the more easily made tests for the principal ingredients of these preparations. Complete analysis will rarely be attempted. The following table, taken from the Druggist's Circular of June, 1910, may be helpful.

DIFFERENTIATION OF COCAINE AND ITS SUBSTITUTES.

	Iodine potassium iodide.	Bromine water.	Sodium hydroxide.	Potassium permanganate.
Eucaine — a.	Yellow-maroon precipitate, soluble on boiling.	Yellow precipitate, soluble on heating.	White precipitate, insoluble in excess and on boiling.	Violet precipitate, blackening quickly.
Eucaine — b.	Deep-red precipitate, soluble on boiling.	Yellow precipitate, slightly soluble on heating, reprecipitated white on boiling.	White precipitate, insoluble in excess and on boiling.	No precipitate immediately; color persists for a day.
Cocaine........	Yellow-maroon precipitate, soluble on boiling.	Yellow precipitate, soluble on heating.	White precipitate, insoluble in excess and on boiling.	Violet precipitate, color persists for one hour, then deposits MnO_2.
Novocaine.....	Deep-red precipitate, soluble on boiling.	Yellow precipitate, soluble on heating.	White precipitate, insoluble in excess and on boiling.	Violet precipitate, blackening quickly.
Stovaine.......	Deep-red precipitate, soluble on boiling.	Yellow precipitate, soluble on heating.	White precipitate, insoluble in excess; aromatic odor on boiling.	Violet precipitate, blackening almost immediately.
Nirvanin.......	Deep-red precipitate, soluble on boiling.	Yellow precipitate, soluble on heating, but the liquid becomes red and gives an agreeable fruity odor.	Precipitate, very soluble in excess of the reagent.	Precipitate, first maroon, then brown.
Alypin.........	Yellow-maroon precipitate, insoluble on boiling; orange-red deposit.	Yellow precipitate, soluble on gentle heating.	White precipitate, insoluble in excess and on boiling.	Bluish-violet precipitate, slowly blackening.

CHAPTER XX.

TEETH AND TARTAR.

THE chemical examination of teeth and tartar, while coming more properly under the head of physiological chemistry, will be considered in part in this place, as the tests made, especially on tartar, are practically all microchemical. The composition of the cement is practically that of true bone, the dentine and enamel differing principally in the proportion of organic matter which they contain. In all of these the presence of lime, phosphoric acid, carbonic acid, and traces of magnesium and calcium fluoride may be demonstrated. The tartar contains a greater proportion of carbonic acid, less calcium phosphate, and much less organic matter than the teeth, taken as a whole, or than dentine, but about the same as enamel. According to Berzelius, sodium chloride and sodium carbonate may also be found.

The composition of the different parts of the tooth substance has been given as follows:

	Organic Matter.	Ash.	$Ca_3(PO_4)_2$.	$MgHPO_4$.	$CaCO_3$.
Dentine...................	23.2	76.8	70.3	4.3	2.2
Cement...................	32.9	67.1	60.7	1.2	2.9
Enamel...................	3.1	96.9	90.5	traces	2.2

Also traces of magnesium carbonate, calcium sulphate, fluorides, and chlorides. An increase in the percentage of calcium phosphate of fluoride increases the hardness of the tooth, while an increase of calcium carbonate decreases the hardness.

Potassium sulphocyanate, ferric phosphate, sulphites, and uric acid have been found in tartar, as additional chemical constituents, while after the solution of the mineral matter

189

the presence of epithelium cells, mucus, and the leptothrix may be demonstrated by the microscope.

According to Vergness, *Du tartre dentaire*, quoted by Gamgee, the tartar from incisor teeth and that from molars show decided difference in their content of iron and calcium phosphates, the analysis being as follows:

	Tartar of Incisors.	Tartar of Molars.
Calcium phosphate	63.88–62.56	55.11–62.12
Calcium carbonate	8.48– 8.12	7.36– 8.01
Phosphate of iron	2.72– 0.82	12.74– 4.01
Silica	0.21– 0.21	0.37– 0.38
Alkaline salts	0.21– 0.14	0.37– 0.31
Organic matter	24.99–27.98	24.40–24.01

DEPOSITION OF TARTAR UNDER VARIOUS SYSTEMIC CONDITIONS.

The presence of oxalates and urates have been reported in the black tartar from pyorrhea cases. The deficient oxidation and high acidity usually occurring in such cases is conducive to the production of large amounts of oxalic or uric acids in the system, not necessarily on the teeth, whether these substances have etiological relations to pyorrhea or not.

The formation of ordinary hard tartar consisting principally of phosphate and carbonate of calcium is accounted for by Dr. Percy G. Howe * as follows: An excess of calcium salts in the blood must be granted as one of the causes of calcification. These calcium salts are held in solution by two distinct factors: first, the excess of carbon dioxide; and second, by the presence of colloidal substances in suspension. This accounts for the fact that the loss of carbon dioxide does not universally precipitate the lime salts. Barille holds that calcium phosphate occurs in the blood as an unstable carbon phosphate which tends to decompose into calcium acid phosphate and bicarbonate, and that

* Dental Cosmos, 1915, page 307.

in saliva we find both these salts held in solution by carbon dioxide as follows:

$$Ca_3(PO_4)_2 + 4\,H_2CO_3 = H_2O + P_2O_8Ca_2H_2.2\ CO_3(CO_3H)_2Ca.$$
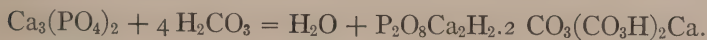
Upon the escape of the carbon dioxide, the calcium precipitates as the tri-metallic phosphate if the solution is alkaline, and as dicalcic phosphates if the solution is acid; and, of course, the loss of carbon dioxide will at the same time result in the precipitation of the neutral carbonate $(CaCO_3)$.

That the general systemic condition is also a factor in the deposition of tartar is indicated by the experience of Dr. Wright of the Harvard Dental School, who has watched for a succession of years the fairly uniform increase in tartar deposits from October to June, and has found the vacation period marked by smaller amounts of deposit.

Lactic and other organic acids have been found in minute quantities in tartar, but these as well as the qualitative tests for urates will be considered more in detail under the Chemistry of Saliva.

Analysis of Teeth and Tartar.

The substance for analysis should be reduced to a moderately fine powder by crushing in a mortar and a fair sample of the whole taken for each test.

Moisture may be detected by the closed-tube test (page 105) and may be determined by accurately weighing out one gram of the substance in a counterpoised platinum dish or crucible and drying at 100° C. to constant weight.

Inorganic matter may be determined by careful ignition of dried substance; raise the temperature slowly till full red heat is reached; cool in a desiccator and weigh.

Organic matter may be ascertained by difference.

Lactates and other organic acids may be detected by careful crystallization and examination with the micropolariscope.

The several inorganic constituents may be demonstrated as follows:

Phosphoric Acid. — Dissolve a little of the powdered substance in dilute nitric acid; then to a few drops of the clear solution add an excess of ammonium molybdate in nitric acid. A yellow crystalline precipitate of ammonium phosphomolybdate will separate. Avoid heating above 60° C., as the ammonium molybdate may decompose and precipitate a yellow oxide of molybdenum.

Carbonic Acid may be detected by liberation of carbon dioxide and passing the gas into lime-water as described on page 93 or with closed tube and drop of baryta-water, page 105.

Chlorine may be detected in the dilute nitric acid solution by the usual silver nitrate test.

Calcium and Magnesium may be separated and identified by the usual methods of analysis in the presence of phosphates.

Test for calcium and magnesium as follows: Add to the hydrochloric acid solution an excess of ammonia; calcium phosphate and magnesium phosphate are precipitated, white. Filter and to the filtrate add ammonium oxalate; a white precipitate shows lime, not as phosphate. Wash the precipitate produced by ammonium hydroxide, dissolve in dilute hydrochloric acid, and add ferric chloride carefully till a drop of the solution gives, when mixed with a drop of ammonium hydroxide, a yellowish precipitate. Nearly neutralize with sodium carbonate and add barium carbonate, which precipitates ferric phosphate. Filter, heat the filtrate, precipitate the barium with dilute sulphuric acid, and filter again. From the filtrate calcium is precipitated as white calcium oxalate by making it alkaline with ammonium hydroxide and adding ammonium oxalate as long as a precipitate is formed. Filter and add to the filtrate sodium phosphate, which precipitates magnesium as ammonio-magnesium phosphate, white.

Laboratory Exercises may consist of the examination by microchemical methods of one or more samples of tartar.

PART V.

ORGANIC CHEMISTRY.

CHAPTER XXI.

THE HYDROCARBONS AND SUBSTITUTION PRODUCTS.

OUR work up to this point has been confined to inorganic chemistry excepting a few microchemical tests for organic substances.

We are now to consider briefly the organic compounds which will serve as a basis for the intelligent study of physiological chemistry, and also some which are of peculiar interest in dentistry.

We shall touch but lightly on some of the subdivisions of the subject and take up a little organic chemistry proper, a little physiological chemistry, a little pathological chemistry, and from it all pick out such facts as may help us to a better understanding of the problems of dentistry.

As in many other departments of science, absolute rules for classification are impracticable; yet we may consider in a general way that the organic compounds are those containing carbon as a molecular constituent. The old conception that the organic compound must have been produced by a vital process of some sort (animal or vegetable) is of little value unless we confine our thought to substances found in nature only.

The compounds of carbon are practically innumerable and very widely distributed, constituting the great bulk (aside from water) of all vegetable or animal substances.

The carbon compounds contain the elements of carbon and hydrogen, and when these two only are present they are *hydro-*

carbons. They more frequently contain carbon, hydrogen, and oxygen, and when the hydrogen and oxygen are present in the proportions in which they occur in water, the compound is a *carbohydrate* (with exceptions).

In the chemistry of the animal body the majority of substances which we meet contain carbon, hydrogen, oxygen, and nitrogen and often in addition sulphur or phosphorus. Many other elements, notably the halogens, and often the metals, may be found in organic compounds.

The question of its composition is then the first one presenting itself in the consideration of an organic substance.

The analysis of organic bodies may be made from two distinct standpoints: first, to determine the various substances which may be separated from a given organized body, as from some part of a plant; secondly, to determine the constituent elements of one of the substances so separated.

As an example of the first sort of analysis, we may find in a potato a certain basic principle (alkaloid), more or less water, and considerable starch. These may be called proximate principles, and the separation of them would be proximate analysis, while the second sort of analysis determines the composition of the starch molecule and is known as ultimate analysis.

QUALITATIVE TESTS.

Carbon. — The presence of this element may be shown by the " carbonization " obtained in the preliminary test, as given on page 104.

Hydrogen shows itself by the production of moisture in these same tests.

Nitrogen may or may not be indicated by the preliminary test. It may be detected with certainty by either of the following methods:

(*a*) Conversion into a cyanogen compound.

A small piece of thoroughly dried albumin together with a little metallic potassium is placed in a matrass, such as is described on page 34, and heated to redness for a few minutes. (Metallic sodium will work as well in most cases.) An alkali cyanide, which may be dissolved in water after breaking the tube, is formed, and by addition of a little yellow ammonium sulphide and evaporation to dryness on a water-bath will be changed to sulphocyanate, NH_4CNS. If the dry residue is taken up with dilute hydrochloric acid, filtered, and tested with a drop of ferric chloride solution, the presence of the sulphocyanate is at once shown by the red color produced.

(*b*) Conversion into free ammonia.

Almost any nitrogenous substance may be made to evolve ammonia-gas by simply heating in a test-tube with several times its bulk of soda-lime. Test for ammonia by moistened red litmus paper or by odor. (This test is known as that of Wöhler, also of Will and Varrentrap.)

The Kjeldahl or moist combustion process is much employed as a quantitative method but may be used qualitatively as follows: The substance is heated in an ignition-tube with concentrated sulphuric acid till a clear (not necessarily colorless) solution is obtained. The mixture is cooled, diluted with water, an excess of caustic soda added, and heat applied when ammonia is evolved, which may be detected by litmus paper or by odor.

Sulphur and Phosphorus are first completely oxidized either by fusion of the substance with alkali nitrate and carbonate or by treatment in the wet way with fuming nitric acid or mixture of potassium chlorate and hydrochloric acid. The resulting sulphate or phosphate is detected by the usual qualitative methods (page 95).

A sulphur test may also be made by heating the substance with a little concentrated sodium hydroxide in the test-tube. A little sodium *sulphide*, which may be detected by dropping onto

a bright silver coin or by testing with lead acetate solution, will thus be formed.

Halogens. — Chlorine, bromine, and iodine cannot be detected in organic combinations by the ordinary qualitative test with silver nitrate and dilute nitric acid, but must first be converted into corresponding inorganic haloid salts. This may be done by heating the organic substance strongly with pure lime, when calcium chloride, bromide, etc., which may be dissolved in water and tested in the usual way, will be formed. (See pages 96 and 97.)

A test for chlorine or iodine may also be made by heating with copper oxide on a platinum wire in the Bunsen flame, chlorine giving first a blue then a green color to the flame. Iodine gives a green only (Beilstein).

Test for presence of C, H, and S in dried albumin.

Test for S by the caustic soda test.

Test for P in casein precipitated from milk.

Test a few drops of chloroform for the presence of chlorine.

THE HYDROCARBONS.

The hydrocarbons are organic compounds of carbon and hydrogen only. The simplest of these is marsh-gas or methane (CH_4). The molecule of this substance consists of a single carbon atom with each of its four points of atomic attraction (valence) satisfied by an atom of hydrogen.

$$\begin{array}{ccc} H & & H \\ & \diagdown C \diagup & \\ H & \diagup \diagdown & H \end{array}$$
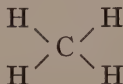
If one of these four atoms of hydrogen is replaced by a chlorine atom, for instance, we have a *substitution product*. Its formula will be CH_3Cl, its name monochlormethane or *methyl chloride*. If two molecules of methyl chloride are brought together and the chlorine removed by metallic sodium the residual

molecules (methyl radicals) will unite, forming a new hydrocarbon, as follows:

$$2\ CH_3Cl + Na_2 = 2\ NaCl + C_2H_6\ \text{(ethane)}.$$

By a similar reaction we may form the third member of the series, C_3H_8 (propane), from ethyl chloride (C_2H_5Cl) and sodium; the fourth member, butane, C_4H_{10}, from propyl chloride, etc. A tabulated list of the first five compounds of this series will plainly show their chemical relationship.

CH_4, methane or methyl hydride (CH_3H).
C_2H_6, ethane or ethyl hydride (C_2H_5H).
C_3H_8, propane or propyl hydride (C_3H_7H).
C_4H_{10}, butane or butyl hydride (C_4H_9H).
C_5H_{12}, pentane or amyl hydride ($C_5H_{11}H$).

Note that the various members of this series differ from one another by CH_2; that is, each higher compound contains one carbon atom and two hydrogen atoms more than its predecessor. This holds true through the series, and the compounds of this or any such series are termed homologues and the series homologous series. Note further that any member of this series (which is known as the paraffin series) may be represented by the general formula C_nH_{2n+2}. This likewise holds true throughout the series, and a compound having sixty carbon atoms will have a formula of $C_{60}H_{122}$. The first four hydrocarbons of this series are gaseous at ordinary temperatures; from C_5H_{12} to about $C_{16}H_{34}$ the hydrocarbons are liquid; from $C_{16}H_{34}$ (melting at about 18°) up they are solids.

Isomers. — When two or more compounds are of exactly the same molecular composition, or when two compounds have the same percentage composition the one being a multiple of the other, the compounds are said to be isomers or isomeric compounds.

The isomerism of the first class is said to be metameric when

the atoms of the several compounds are not only the same in kind, but also the same in the number of each kind. For example, $C_{12}H_{22}O_{11}$ is the formula for cane sugar; $C_{12}H_{22}O_{11}$ is also the formula for milk sugar, and these two compounds have decidedly different properties, the difference being dependent upon the arrangement or relationship of the atoms in the molecule. Another example illustrating this difference may be found in the graphic formula for normal and isobutane given below.
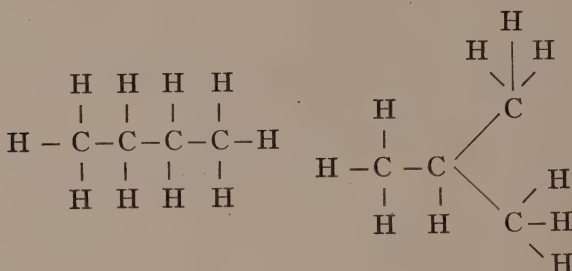
Note that each molecule has an empirical formula of C_4H_{10}; the normal compound may be represented as $CH_3.(CH_2)_2.CH_3$, the iso-compound as $CH_3.CH.(CH_3)_2$. These will be found to have quite different physical and chemical properties.

The isomerism of the second class is called polymeric and one substance is the polymer of another when the molecules are of the same percentage composition but of different molecular weights, for example, CH_2O is gaseous formaldehyde, $(CH_2O)_3$ is its polymer or polymeric form, known as paraform, a white crystalline solid.

The hydrocarbons of the paraffin series are known as *straight chain* or *aliphatic hydrocarbons*, their graphic formulæ consisting of " chains " of carbon atoms, as butane, $-C-C-C-C-$, in distinction from the closed-chain or cyclic compounds as repre-

sented by the "benzene-ring" (page
244) carbon nucleus with the carbon
atoms united in a continuous *closed*
chain or "cycle."

The paraffins are called saturated
hydrocarbons because they are inca-
pable of forming *addition* products by
absorption of chlorine, for instance,
without first giving off an equivalent
number of atoms of hydrogen. This
is because of the complete "satura-
tion" or union of every carbon
"bond" with some other atom.*
Paraffin wax and mineral oil are mix-
tures of saturated hydrocarbons and
resist chemical action even of strong
nitric acid or sulphuric acid.

The name paraffin is derived from
the two Latin words *parvus*, little, and
affinitas, affinity.

The natural sources of hydrocar-
bons of the paraffin series are natural
gas and crude petroleum, or rock oil.
Many of these hydrocarbons exist as
such in the petroleum, and some un-
doubtedly are produced by the heat
used to effect a separation of the va-
rious compounds. This separation
may be effected by distilling the oil
in an apparatus similar to that pic-
tured in Fig. 17, and is known as

* Notice that while addition products of
saturated hydrocarbon cannot be formed, sub-
stitution products are easily possible. See
page 203.
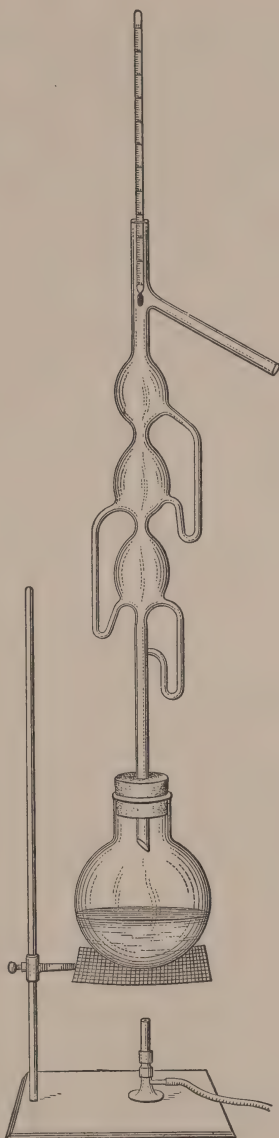
FIG. 17.

fractional distillation, the different hydrocarbons passing over at different temperatures. Separation by this method, however, is by no means complete, and the resulting products are themselves mixtures of hydrocarbons, and are distinguished by physical properties rather than by chemical composition.

When crude petroleum is thus distilled, the following products are obtained: first, rhigoline, which comes over at a temperature of $20°$ to $22°$ C.; then petroleum ether or benzine at from $50°$ to $60°$ C.; then gasolene or naphtha at about $75°$ C.; then one or two unimportant commercial products, and kerosene or burning oil is obtained at $150°$ to $250°$ C. Above this, we may obtain paraffin oil or light lubricating oils; then the heavy lubricating or cylinder oils, and from the residue we obtain the solid substances known as vaseline or petroleum jelly and paraffin of various degrees of hardness.

The first five hydrocarbons of this series we will consider somewhat in detail, not only because they are important and comparatively common, but also because they serve as types of all other compounds of the series, and reactions which we study with these compounds are, as a rule, general typical reactions which may be produced with other members of the series.

Methane, CH_4, occurs as marsh gas in stagnant ponds or pools and is a constituent of " fire damp " in coal mines. It is a colorless gas, odorless when pure, and very slightly soluble in water. It may be prepared artificially by the decomposition of anhydrous sodium acetate, with sodium hydroxide and lime. See reaction on page 382, Exp. 63. Methane burns in the air with the production of carbon dioxide and water

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O.$$
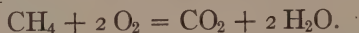
Ethane, C_2H_6, the second member of the series, occurs naturally in a solution in crude petroleum, and can be artificially prepared by the electrolytic decomposition of a saturated solution of potassium acetate as follows:

$$2\,CH_3COOK = C_2H_6 + 2\,CO_2 + K_2.$$

The free potassium, of course, decomposes water, liberating hydrogen gas which collects at the negative pole, and, if the solution contains sufficient potassium hydroxide, the carbon dioxide will be dissolved, allowing ethane to collect at the positive pole.

Ethane may also be made from a haloid derivative of marsh gas by the action of metallic sodium; that is, in CH_4 we may replace one of the hydrogen atoms with iodine, forming CH_3I, methyl iodide; then by treatment with metallic sodium, the following reaction will take place:

$$2\,CH_3I + 2\,Na = C_2H_6 + 2\,NaI.$$

Ethane is slightly more soluble in water than methane. It may be condensed to a liquid at a pressure of forty-six atmospheres.

Propane, C_3H_8, also occurs in petroleum, and can be made by treating a mixture of ethyl iodide and methyl iodide with metallic sodium:

$$C_2H_5I + CH_3I + 2\,Na = C_3H_8 + 2\,NaI.$$

This is a general method for building up hydrocarbon compounds. Propane at ordinary atmospheric pressure is condensed to liquid at 17° below zero.

Butane, C_4H_{10}, is the first of the series capable of existing in two forms, isomers. The structural formulæ of these two compounds are shown in the illustration of the term isomer on page 198. This compound and many of its higher homologues are of importance only in relation to some of their derivatives which will be subsequently studied.

Unsaturated Hydrocarbons.
DOUBLE-BONDED HYDROCARBONS.

When a mixture of alcohol and strong sulphuric acid is heated, with the acid in considerable excess, water is with-

drawn from the molecule of alcohol, and a gas found to have the formula C_2H_4 is produced. (See Exp. 64.) The name of this gas is ethylene; it occurs in coal gas and in traces in solution in crude petroleum. It is the first of a series of hydrocarbons which contain double-bonded carbon atoms. The double bond is assumed because it is found to be impossible to produce a lower compound of this series, such as CH_2, which might be called methylene, but which would necessitate a bivalent carbon atom; also because the hydrocarbons of this series are capable of formation of addition products as well as of substitution products.

Note that the formula of ethylene does not conform to the general formula of the paraffins (C_nH_{2n+2}), but is the first member of the new series of " unsaturated " hydrocarbons; the olefin or ethylene series with a general formula of C_nH_{2n}.

The hydrocarbons of this series take their names from corresponding members of the paraffin series, with " ene " as a distinguishing termination — ethylene, C_2H_4, propylene, C_3H_6, butylene, C_4H_8, etc. They are unimportant in dental or physiological chemistry. Some of the higher oxygenated compounds of this class are, however, of great importance, as olein, which is a constituent of vegetable and animal fats and oils.

TRIPLE-BONDED HYDROCARBONS.

A third series of the straight chain hydrocarbons is the acetylene series; these are triple bonded, and of course unsaturated, with a general formula of C_nH_{2n-2}.

The only members of this series of special interest are, first, *acetylene*, $H-C \equiv C-H$, (C_2H_2), made from calcium carbide and water (see Exp. 67, page 382). It is poisonous, combining directly with the hemoglobin of the blood, has a disagreeable odor, and is inflammable; second, *allylene*, C_3H_4, derivatives of which occur in onions, garlic, mustard-oil, etc.

Haloid Derivatives of the Paraffins.

Methane furnishes three chlorine substitution products which are more or less in common use: first, the monochlor-methane, or methyl chloride; second, the trichlor-methane $CHCl_3$ or chloroform, and third, the tetrachloride of carbon CCl_4.

Methyl Chloride, CH_3Cl, may be made from methyl alcohol, zinc chloride, and hydrochloric acid. It is a colorless gas, condensing to a liquid at $23°$ C.; used as a spray in producing local anesthesia (page 182); also as a constituent of anesthetics, such as anesthol, somnoform, etc.

Dichlor-methane, CH_2Cl_2, also known as methylene chloride, has been used as a general anesthetic usually mixed in more or less chloroform and alcohol. Its use in this way is open to criticism because of its poisonous action, affecting the heart.

Chloroform, $CHCl_3$, trichlormethane, is a general anesthetic prepared by distilling a mixture of chlorinated lime and acetone. Alcohol and water were formerly used in place of acetone (see Exp. 70, page 383). While it is not regarded as inflammable, its heated vapor can be made to burn with a greenish flame. The reaction with alcohol is probably as follows: $4 \ C_2H_5OH + 8 \ Ca(ClO)_2 = 2 \ CHCl_3 + 3 \ Ca \ (CHO_2)_2 + 5 \ CaCl_2 + 8 \ H_2O$.

Methyl Chloroform, CH_3CCl_3, formed by replacing the hydrogen atom of chloroform by a methyl group, CH_3, has been used as an anesthetic.

Tetrachloride of carbon is a colorless liquid used quite largely as a solvent. It also has anesthetic properties but like dichlormethane, is dangerous because of its action on the heart.

Methyl bromide, or monobrom-methane, is used to some extent as a constituent of anesthetics.

Bromoform, $CHBr_3$, tribrom-methane, is prepared from bromine and a solution of alcoholic potash. Its properties are similar to those of chloroform, but it is more poisonous.

Methyl Iodide, CH_3I, is a heavy liquid, with pleasant odor, boiling-point $43°$ C.; has been used somewhat as a vesicant.

Iodoform, CHI_3, tri-iodomethane, is a much-used and very valuable antiseptic. It is a light-yellow crystalline powder with characteristic persistent odor (Plate V, Fig. 1, page 2c4).

Iodoform may be made by heating in a retort two parts of potassium carbonate, two of iodine, one of strong alcohol, and five of water, till the mixture is colorless,

$$C_2H_5OH + 4\ I_2 + 3\ K_2CO_3 = CHI_3 + KCHO_2 + 5\ KI + 2\ H_2O + 3\ CO_2.$$
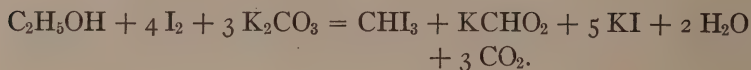
Iodoform is also produced from action of the above reagents with acetone in place of alcohol. This test is a very delicate one and advantage is taken of it in testing for acetone in saliva, which see.

Cacodyl is an example of the arsenic derivatives of the hydrocarbons. It is one of several products which result from the distillation of a mixture of potassium acetate and white arsenic. Its composition is that of dimethylarsine, $(CH_3)_2As$.

Ethyl Chloride, C_2H_5Cl, chlorethyl, may be made by distillation of a mixture of alcohol and hydrochloric acid and purification of the distillate. It is extremely inflammable, boils at $12°$ C., and is used as a local anesthetic in similar manner to methyl chloride. Its higher boiling-point makes it the more convenient of the two preparations (see page 178).

Ethyl Bromide, C_2H_5Br, prepared from alcohol, sulphuric acid, and potassium bromide. It is a heavy colorless liquid, does not burn, and has been used to considerable extent as a general anesthetic.

PLATE V.—ORGANIC CHEMISTRY.
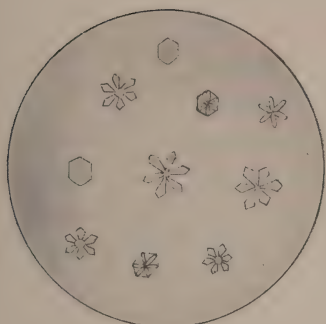
FIG. 1.
Iodoform.
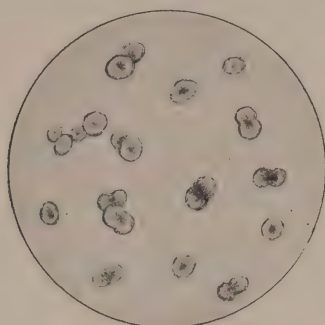
FIG. 2.
Leucin.
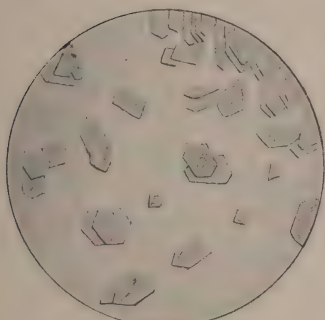
FIG. 3.
Urea Nitrate.
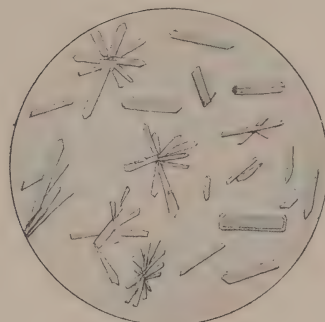
FIG. 4.
Hippuric Acid.

FIG. 5.
Benzoic Acid (sublimed).
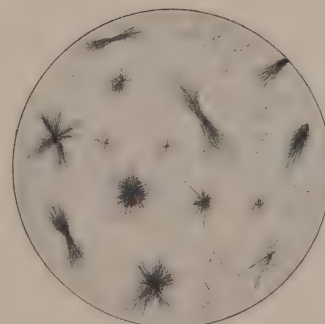
FIG. 6.
Tyrosin.

CHAPTER XXII.

ALCOHOLS.

If we substitute for one of the hydrogen atoms of methane, a hydroxyl group (OH), we shall produce the first of a series of alcohols, several of which will claim our attention.

The alcohols may be considered as hydroxides of alkyl * radicals, CH_3OH being methyl alcohol; C_2H_5OH being ethyl or ordinary alcohol; C_3H_7OH being propyl alcohol; and $C_5H_{11}OH$, amyl alcohol or fusel oil.

The alcohols as a class may be prepared by the action of moist silver oxide on the corresponding halogen compounds; e.g.,

$$CH_3Br + AgOH = CH_3OH + AgBr.$$

In many instances, the alkaline hydroxides will act in the same way.

$$CH_3Br + KOH = CH_3OH + KBr.$$

Alcohols treated with metallic sodium or potassium liberate hydrogen gas, forming compounds known as alcoholates; e.g.,

$$CH_3OH + K = CH_3OK + H;$$
or $$C_2H_5OH + K = C_2H_5OK + H.$$

While these compounds are, as just stated, called alcoholates, they may be distinguished, one from another, by using the name of the alkyl radical involved, and CH_3OK will be potassium methylate, while C_2H_5OK will be potassium ethylate.

Alcohols may contain more than one hydroxyl group, and, according to number of the OH groups, are termed mono-, di-,

---

* Alkyl — a term used to denote any hydrocarbon radical as CH_3-, C_2H_5-, C_3H_7-, etc.

tri-atomic, etc. Thus, ordinary alcohol, C_2H_5OH, is mono-atomic; glycol, $C_2H_4(OH)_2$, is diatomic; glycerol, $C_3H_5(OH)_3$, is triatomic, while mannite, $C_6H_8(OH)_6$, is a hexatomic alcohol.

Alcohols may also be classified according to the relative position of the hydroxyl group. By this classification, we may have primary alcohols with OH replacing a hydrogen of the $-CH_3$ group; secondary alcohols with OH replacing the hydrogen of a $-CH_2$ group; and tertiary alcohol with OH replacing the hydrogen of a $-CH$ group. This may be illustrated by the formula of an alcohol of each class. $CH_3-CH_2-CH_3$, being the hydrocarbon, a primary alcohol will have the formula $CH_3.CH_2.CH_2OH$, and $-CH_2OH$ may be considered distinctive grouping of the primary alcohols. Again from the same hydrocarbon, if OH is substituted for an H of CH_2 then the secondary alcohol will be $CH_3-CHOH-CH_3$ and $-CHOH$ may be regarded as a distinctive group of this class.

The tertiary alcohols, however, must be produced from compounds having at least four carbon atoms, as a CH group is only possible when there are sufficient carbon atoms to produce a forked chain; that is, in a compound with three carbon atoms, one must of necessity be placed between the other two, while with four carbon atoms, the carbons may be attached in a straight chain, such as $C-C-C-C$, or they may be arranged as a forked chain $C-C\diagup^C_{\diagdown C}$, and by supplying the hydrogen atoms necessary to satisfy the valence of each carbon, in this latter chain we find a CH group. OH introduced in place of the hydrogen of this group gives us the tertiary alcohol,

$$CH_3-COH\diagup^{CH_3}_{\diagdown CH_3}$$
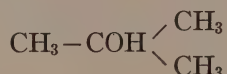
Methyl Alcohol, CH_3OH, $(H-CH_2OH)$,* wood spirit, carbinol, is a product of the destructive distillation of wood or can

* Note that CH_2OH is the "alcohol group" peculiar to this class of alcohols.

be made synthetically from methane. It is a colorless, inflammable liquid, with a gravity of 0.802 at 15° C., with solvent properties similar to ordinary alcohol. It boils at 66°.

Ethyl Alcohol, C_2H_5OH, ($CH_3 - CH_2OH$), methyl carbinol, grain alcohol, or ordinary alcohol may be made by the action of silver hydrate on ethyl iodide or bromide as suggested on page 205. It is made commercially by fermentation of various carbohydrates and purified by distillation. Carbon dioxide is evolved as follows:

$$C_6H_{12}O_6 = 2\ C_2H_5OH + 2\ CO_2.$$

95% alcohol has a specific gravity 0.8164, boils at about 78° C., dissolves many inorganic salts, vegetable waxes, resins (not gums), oils, etc., and is miscible with water, ether, or chloroform.

Propyl Alcohol, normal, $CH_3.CH_2.CH_2OH$, occurs with amyl alcohol as a constituent of fusel oil, or may be prepared by general method with moist silver oxide. It is a colorless liquid, boils at 97° C. The iso-compound, $CH_3.CHOH.CH_3$, may be made by reducing acetone with nascent hydrogen; nascent hydrogen may be produced by sodium amalgam.

Butyl Alcohol, C_4H_9OH, occurs in four isomeric forms. The normal alcohol is $CH_3.(CH_2)_2.CH_2OH$. It is produced by the fermentation of glycerol. It boils at 117° C. The isobutyl alcohol, $(CH_3)_2.CH.CH_2OH$, obtained from fusel oil, boils at 107° C.

Amyl Alcohol, $C_5H_{11}OH$, ($C_4H_9 - CH_2OH$), consists of about 87% of isobutyl carbinol and about 13% of an isomer known as active amyl alcohol. It is a colorless, oily liquid with a specific gravity of 0.818. It boils at about 130° C., and burns with a bluish flame.

Fusel oil, or potato spirit, consists of amyl alcohol carrying traces of various other alcohols as impurities.

Amyl alcohol is a valuable solvent and is largely used in the manufacture of artificial fruit flavors, banana essence, and the like.

Oxidation of the Alcohols.
Aldehydes.

The first step in the oxidation of an alcohol consists not in the addition of oxygen but in the withdrawal of hydrogen; thus the oxidation of methyl alcohol produces formaldehyde (CH_2O) and water.

$$CH_3OH + O = CH_2O + H_2O.$$
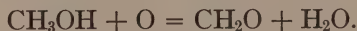
Aldehydes may be considered compounds containing an alkyl radical and a distinctive group, $-C\begin{smallmatrix} \diagup H \\ \diagdown O \end{smallmatrix}$; thus $\begin{smallmatrix} H \\ | \\ CHO \end{smallmatrix}$ is formaldehyde, $\begin{smallmatrix} CH_3 \\ | \\ CHO \end{smallmatrix}$ is acetaldehyde, etc. (Compare Alcohol, page 206.)

Formaldehyde coagulates albumin and hardens gelatin; when used as a preservative it renders the proteins tougher and less digestible.

Formaldehyde polymerizes, producing the paraform or paraformaldehyde of trade, trioxymethylene, with a probable formula of $(CH_2O)_3$. It also forms one lower polymer $(CH_2O)_2$ and at least one higher, formose, a substance allied to glucose.

Acetaldehyde, aldehyde, CH_3-CHO or C_2H_4O, the aldehyde from ethyl alcohol, may be made by addition of H_2SO_4 to a mixture of alcohol and bichromate of potassium. It is a colorless, inflammable liquid with pungent etherial odor and boils at $22°$ C.

Paraldehyde, $(C_2H_4O)_3$, a polymer of acetaldehyde, is a "colorless liquid with a strong pungent odor, soluble in 8.5 parts of water at $15°$ C., miscible in all proportions with alcohol, ether, and fixed or volatile oils." (U. S. P.) It is a valuable hypnotic.

Chloral, CCl_3CHO, trichloraldehyde, is an oily liquid formed by action of dry chlorine gas on pure alcohol; soluble in ether and

chloroform, boiling at from 94° C. to 98° C., and forming, with a molecule of water *chloral hydrate*, $CCl_3CHO.H_2O$, a crystalline solid, and this is the chloralum hydratum of the pharmacopœia (see page 176).

Chloral hydrate is decomposed by sodium or potassium hydrate with liberation of chloroform (see Exp. 87, page 387):

$$CCl_3 - CHO + KOH = CHCl_3 + KCOOH \text{ (potassium formate)}.$$

Upon warming a drop or two of aniline oil in an excess of alcoholic potash, chloral hydrate forms, first, chloroform, then phenylisocyanide, C_6H_5NC, the persistent disagreeable odor of which furnishes a delicate test for chloroform or chloral (see Exp. 88, page 387). By using $CHCl_3$ as the reagent in place of the aniline, the same reaction becomes a test for aniline or organic compounds, from which aniline may be produced by heating with alcoholic potash as acetanilide. Other aldehydes from hexatomic alcohols are dextrose (glucose) and galactose. They are represented by the formula $CH_2OH - (CHOH)_4 - CHO$, and will be considered more fully in a subsequent lecture.

Ketones.

The oxidation of *secondary* alcohols (page 206) will not yield aldehydes, but a class of substances known as *ketones :*

$$(CH_3)_2 - CH - CHOH - CH_3 + O = (CH_3)_2 - CH - C : O - CH_3 + H_2O,$$

A secondary alcohol.
Methyl isopropyl carbinol.

Methyl isopropyl ketone.

or $\quad CH_3 - CHOH - CH_3 + O = CH_3 - CO - CH_3 + H_2O.$

Isopropyl alcohol.

Dimethyl ketone.
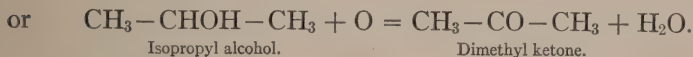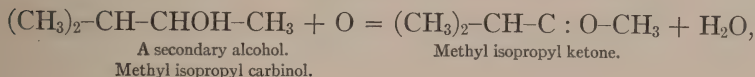
The converse of each of these reactions is possible, and, by reduction of a ketone with nascent hydrogen (sodium amalgam), the secondary alcohol will be formed:

$$CH_3 - CO - CH_3 + H = CH_3 - CHOH - CH_3.$$

Acetone.

Isopropyl alcohol.
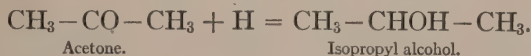
Likewise primary alcohols may be produced by the reduction of aldehydes:

$$CH_3-CHO + H_2 = CH_3-CH_2OH.$$
<p style="text-align:center;">Acetaldehyde.   Ethyl alcohol.</p>
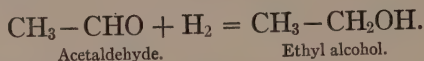
Note that the grouping peculiar to ketones is $= CO$ or $-CO-$.

Acetone, or dimethylketone, $CH_3-CO-CH_3$, a colorless liquid of peculiar odor, boils at 56° C. and is made commercially by the dry distillation of acetate of lime.

It occurs in the blood and urine of patients suffering from advanced diabetes. According to von Noorden, the acetone found in the blood is formed by an intracellular process and indicates an acid auto-intoxication and an insufficient *utilization* of carbohydrates. In the experience of the author, acetone may sometimes be found in the saliva when it cannot be found in the urine (for test, see Acetone under Saliva and Urine).

Another ketone of interest is levulose, fruit-sugar, $CH_2OH-CHOH.CHOH.CHOH.CO.CH_2OH$, which, with glucose, will be studied later.

While the oxidation of a primary alcohol will produce an aldehyde and the oxidation of a secondary alcohol will produce a ketone, the tertiary alcohol, by action of an oxidizing agent, is split into two new carbon compounds, that is, the chain is broken and simpler compounds usually including an organic acid are formed.

CHAPTER XXIII.

ETHERS.

ETHERS may be regarded as oxides of the hydrocarbon radicals, as $\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\Big\rangle O$, or as anhydrides of the monatomic alcohols, water having been removed from two molecules of the alcohol:

$$2\,C_2H_5OH - H_2O = (C_2H_5)_2O.$$

Ethers may be simple, mixed, or compound. The simple ether is illustrated above by the formula for ordinary or ethyl ether, where two radicals of the *same* kind are united by an atom of oxygen.

In a mixed ether, these radicals will be of different kinds; as, for example, $CH_3 - O - C_2H_5$, methyl-ethyl ether.

The compound ethers are compounds of alcohol radicals with acid radicals, that is, the salts of alcohol radicals. The acid may be either organic or inorganic; thus, we have nitric ether, ethyl nitrate, $C_2H_5NO_3$, and we have acetic ether, ethyl acetate, $C_2H_5C_2H_3O_2$. The compound ethers are often called esters and form a large and important class of organic compounds.

A general method for the preparation of simple and mixed ethers is that of distillation of the corresponding alcohols with sulphuric acid, as illustrated by experiment No. 94, page 388. They may also be produced by the action of silver oxide on the corresponding alkyl iodides:

$$2\,C_2H_5I + Ag_2O = (C_2H_5)_2O + 2\,AgI,$$
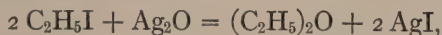
also, by treating the sodium alcoholate with an alkyl iodide,

$$C_2H_5ONa + C_2H_5I = (C_2H_5)_2O + NaI$$

or $\qquad CH_3ONa + C_2H_5I = \begin{matrix} CH_3 \diagdown \\ O + NaI. \\ C_2H_5 \diagup \end{matrix}$
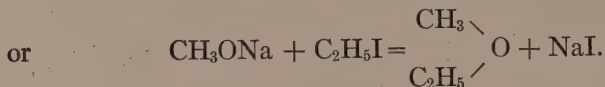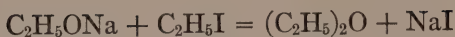
Methyl Ether. — Methyl oxide, $(CH_3)_2O$, also known as formic ether, is isomeric with ordinary alcohol, and may be made in a manner similar to that used in the production of ethyl ether (*q.v.*). At ordinary temperature it is a gas, but liquefies at $-20°$ C. (Bernthsen). It has been used as a general anesthetic, and the anesthesia is said to be profound and quickly produced (U. S. D. from A. J. P., Sept., 1870).

Methyl-ethyl Ether. — This name, besides indicating a definite compound as referred to in the preceding paragraph, has been applied to a mixture of methyl ether and ethyl ether, used for purposes of general anesthesia.

Methylene Ether. — A name applied to a mixture of methylene dichloride and ethyl ether, used as an anesthetic, but it has been found unsafe (U. S. D.).

Ethyl Ether. — Ethyl oxide, $(C_2H_5)_2O$. The ether used for general anesthesia should contain not less than $95\frac{1}{2}\%$ or more than $97\frac{1}{2}\%$ of ethyl oxide, the remainder consisting of alcohol with a little water (U. S. P.). It is a light colorless liquid with a specific gravity of 0.715 at $25°$ C., with a boiling-point of about $35°$ C. It may be made by the action of sulphuric acid on ethyl alcohol, and from this fact has been known as sulphuric ether, but this name is, of course, incorrectly used, sulphuric ether being properly an ethyl sulphate, $(C_2H_5)_2SO_4$.

In the preparation of ether, sulphuric acid may be mixed with rather more than its own bulk of alcohol, the mixture heated to a temperature of from $130°$ to $138°$ C. in a suitable retort or still, the distillate (ether) being collected in a *cold* receiver.

The reaction takes place in two steps, as follows: One molecule of acid and one of alcohol react to form ethyl sulphuric

acid (ethyl acid sulphate) and H_2O, $H_2SO_4 + C_2H_5OH = C_2H_5HSO_4 + H_2O$. Then the ethyl sulphuric acid reacts with a second molecule of alcohol to form ether and sulphuric acid, $C_2H_5HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4$. Thus the sulphuric acid, from two molecules of alcohol, has produced one molecule of ether and is in condition to repeat the process, having been changed only to the extent of adulteration with one molecule of water. In accordance with this theoretic formation of ether by simple dehydration of alcohol by sulphuric acid, provision is made for a continuous process, by the introduction of a constant supply of fresh alcohol into the retort during the distillation, and so regulated that the total bulk of liquid is neither increased nor diminished. The product is then purified, and freed from water and traces of acid by redistillation over a mixture of lime and calcium chloride.

Ether, according to the U. S. P. requirements, is " a transparent, colorless, mobile liquid with characteristic odor and a burning and sweetish taste."

It is soluble in about twelve times its volume of water and in all proportions in alcohol, chloroform, petroleum ether, benzene, and oils. It is readily inflammable, and this fact, together with its easy volatility, makes it necessary to use considerable care when handling it.

The action of sulphuric acid upon alcohol needs careful regulation; because there may be produced three other products in addition to the ethyl oxide already considered. These are, first, ethyl sulphuric acid, $C_2H_5HSO_4$; second, ethyl sulphate $(C_2H_5)_2SO_4$, these being respectively the acid and neutral ethyl esters of H_2SO_4; third, the hydrocarbon *ethylene*, C_2H_4. This latter compound is the first of the ethylene series of hydrocarbons with the general formula C_nH_{2n} and containing " double-bonded " carbon atoms, $\begin{smallmatrix} H \searrow & & \nearrow H \\ & C = C & \\ H \nearrow & & \searrow H \end{smallmatrix}$ or $CH_2 = CH.CH_3$.

These are unsaturated hydrocarbons (see page 201). Ethylene is produced by the action of an excess of concentrated sulphuric acid, which abstracts water from each molecule of alcohol ($C_2H_5OH - H_2O = C_2H_4$), whereas in the preparation of ether the more dilute acid abstracts water from *two* C_2H_5OH.

Compound Ethers or Esters.

Ester is the term applied to etherial salts; that is, compounds in which an alkyl group has taken the place of replaceable hydrogen of the acid. They are produced by the action of the acid upon the alcohol which is as nearly as possible free from water.

Such action by the halogen acids would produce the alkyl haloids already considered; for example, $CH_3OH + HCl = CH_3Cl + H_2O$. As the water produces alcohol and hydrochloric acid by action on CH_3Cl it must be removed as the experiment proceeds.

The ethyl hydrogen sulphate is produced as an intermediate step in the preparation of ether, *q.v.*

Ethyl nitrite, $C_2H_5NO_2$, is a colorless liquid, boiling at 17° C. and is used in medicine as Sweet Spirits of Niter, which is an alcoholic solution containing traces of the ethyl nitrate, various oxidation products, and not less than 3.5% nor more than 4.5% of the ethyl nitrite. It is insoluble in water, but by action of boiling water or dilute alkalies becomes ethyl alcohol, $C_2H_5NO_2 + KOH = C_2H_5OH + KNO_2$. See Exp. 97.

Ethyl Acetate, $CH_3-COO.C_2H_5$, is formed by heating ethyl alcohol, sulphuric acid, and acetate of sodium. This reaction constitutes a qualitative test for acetic acid or acetates, the odor of the ester being sufficiently characteristic to furnish a delicate test (page 100).

The acetic ether of the U. S. P. is "a liquid composed of about 98.5% of ethyl acetate and 1.5% alcohol."

Ethyl Butyrate, $CH_3-CH_2-CH_2-COOC_2H_5$. This ester dissolved in ten parts of alcohol forms pineapple essence. It

may be made in a manner similar to the preparation of ethyl acetate, i.e., by heating together alcohol, butyric acid, and concentrated sulphuric acid. The production of the ester is likewise used as a qualitative text for the presence of the acid, and employed in the examination of gastric contents as follows: " Heat 10 c.c. of contents with 5 c.c. of strong sulphuric acid and 4 c.c. of 95% alcohol; odor of pineapple indicates butyric acid." (Hewes.)

Amyl Acetate and Amyl Butyrate may be obtained by heating the respective acids with amyl alcohol ($C_5H_{11}OH$) and strong sulphuric acid. These esters may also be used in detecting the presence of the acid, amyl alcohol being used in place of ordinary alcohol. Amyl acetate gives the odor of pears, amyl butyrate that of bananas.

Amyl nitrite, $C_5H_{11}NO_2$, is a compound used in medicine to a considerable extent, usually administered by inhalation. The U. S. P. preparation contains about 80% of amyl nitrite. It is very soluble and inflammable.

Fats are esters of glyceryl, C_3H_5, also called tritenyl, propenyl, etc. This radical forms with hydroxyl (OH) the propenyl alcohol, $C_3H_5(OH)_3$, which is ordinary glycerin or glycerol.

Glyceryl butyrate or butyrin, $CH_3-(CH_2)_2-COOC_3H_5$, constitutes (together with smaller quantities of the glyceryl esters of capric, caproic, and caprylic acids) about 7% of butterfat. These esters are readily saponified by treatment with alcoholic potash; then, by decomposition of the potassium salts with H_2SO_4, the acids, being volatile, may be separated by distillation. The amount of volatile fat acids thus obtained is a valuable test for the genuineness of the butter.

For further consideration of fats see Chapter **XXXI**.

CHAPTER XXIV.

ORGANIC ACIDS.

IF the oxidation of an alcohol is carried beyond the formation of aldehyde or ketone, i.e., if the aldehyde or ketone be oxidized, an organic acid results. The first atom of oxygen involved in this process does not become a constituent part of the new molecule, but simply withdraws hydrogen from the old (the alcohol), as shown in the formation of aldehydes on page 208. The second atom of oxygen, however, attaches itself to the molecule and does become a part of the new substance (the acid):

$$\underset{\text{Alcohol.}}{\overset{\text{CH}_3}{\underset{|}{\text{CH}_2\text{OH}}}} + O = \underset{\text{Aldehyde.}}{\overset{\text{CH}_3}{\underset{|}{\text{CHO}}}} + H_2O \quad \underset{\text{Aldehyde.}}{\overset{\text{CH}_3}{\underset{|}{\text{CHO}}}} + O = \underset{\text{Acid.}}{\overset{\text{CH}_3}{\underset{|}{\text{COOH}}}}$$
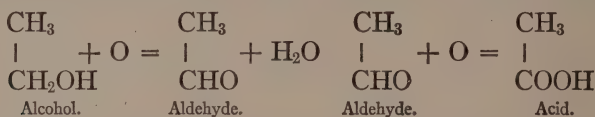
The group $-COOH$ is known as carboxyl and is the characteristic group of the acids. The hydrogen of the carboxyl differs from the other atoms of hydrogen in the molecule in that it is united to oxygen rather than to carbon, and constitutes the basic or replaceable hydrogen of the acid; hence acetic acid is monobasic, and the only possible salt of potassium, for instance, is CH_3-COOK.

The basicity of the acid depends on the number of *carboxyl* groups it contains.

Among the monobasic acids of the fatty or paraffin series which we will study are the following:

Representative Fatty Acids.

H.COOH = formic acid or hydrogen formate;
CH_3.COOH = acetic acid or hydrogen acetate;

$C_2H_5.COOH$ = propionic acid or hydrogen propionate;
C_3H_7COOH = butyric acid or hydrogen butyrate;
C_4H_9COOH = valeric acid or hydrogen valerate;
$C_{15}H_{31}COOH$ = palmitic acid or hydrogen palmitate;
$C_{17}H_{35}COOH$ = stearic acid or hydrogen stearate.

The acids of these series are represented by the general formula $C_nH_{2n}O_2$. They all are monobasic; i.e., they contain only one atom of replaceable hydrogen.

Formic Acid, ($H.COOH$), originally distilled from the bodies of ants (formica, from which the name is derived), is a colorless, easily volatile liquid. It may be prepared in the laboratory by heating oxalic acid with glycerol, when the oxalic acid breaks up into formic acid and CO_2.

$$C_2H_2O_4 = CO_2 + CHOOH.$$

Carbon monoxide, passed over hot potassium hydroxide, results in the formation of potassium formate,

$$CO + KOH = HCOOK.$$

Also by treatment of ammonium carbonate with nascent hydrogen (sodium amalgam),

$$CO_3(NH_4)_2 + 2\,H = HCOO(NH_4) + H_2O + NH_3$$

and

$$HCOO(NH_4) + NaOH = HCOONa + NH_3 + H_2O.$$
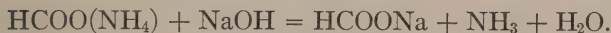
Formic acid, according to the above reaction, is apparently carbonic acid less one atom of oxygen, and the fact that formic acid acts easily as a reducing agent, taking away oxygen from other bodies and becoming H_2CO_3, is further proof of this relationship.

Acetic Acid, CH_3COOH, is obtained commercially by the oxidation of ethyl alcohol. It is the acid of vinegar, which, according to Massachusetts law, should contain $4\frac{1}{2}\%$ of acid. Glacial acetic acid is a commercial name of the acid containing 1% or less of water; it is a colorless solid at a temperature

below 15° C. The U. S. P. acetic contains only 36% (by weight) of the pure acid.

Either one, two, or all three of the hydrogen atoms of the CH_3 group may be replaced by chlorine, forming respectively the mono-, di-, and tri-chloracetic acids, the trichloracetic acid being used to a considerable extent in dentistry (page 187).

Acetic acid, by the abstraction of water, forms an anhydride, $C_4H_6O_3$:

$$2 HC_2H_3O_2 = (C_2H_3O)_2O + H_2O.$$

This substance is of considerable importance in organic reactions. It is a colorless liquid with a boiling-point of 138° C., and, with the halogens, forms compounds such as acetyl choride, C_2H_3OCl, the radical C_2H_3O being known as the acetyl radical.

Propionic acid, $CH_3.CH_2.COOH$, is a colorless liquid, boiling at 140° C. According to Witthaus, it is best prepared by heating ethyl cyanide with caustic potash until the odor of the ester has disappeared:

$$C_2H_5CN + KOH + H_2O = C_2H_5COOK + NH_3.$$

Then, by treatment with H_2SO_4, the propionic acid is liberated, and may be separated by distillation.

Butyric Acid, C_3H_7COOH, occurs as a product of fermentation of butter, or other animal fat containing butyrin; also from the decomposition of lactic acid, two molecules of lactic acid furnishing one of butyric acid, two of carbon dioxide and two of hydrogen (H_2). It is an occasional constituent of the gastric contents, and may be detected by formation of the ethyl ester (page 215). The pure acid is a heavy, colorless liquid with characteristic odor, soluble in water in any proportion. See page 215 for the glyceryl ester of butyric acid (butyrin); also for stearic and palmitic acids.

Valeric Acid, C_4H_9COOH, may be made by the oxidation of amyl alcohol $(C_5H_{11}OH)$. It is an oily liquid boiling at 174° C. It occurs as a constituent of valerian, and in consequence has

been called valeric acid. Its salts are used in medicine as sedatives.

The valeriate of amyl has an odor resembling that of apples, and is used in alcoholic solutions as apple essence.

Palmitic Acid, $C_{15}H_{31}COOH$, a solid " fat acid, " occurs as a glyceryl ester in butter (to a very slight extent), in olive oil, palm oil, and bayberry wax. Combined with certain alcohols it occurs in white and yellow wax; also in spermaceti.

Palmitin, $C_3H_5(C_{16}H_{31}O_2)_3$, occurs in all animal fat and in large quantities in human fat.

Stearic Acid, $C_{17}H_{35}COOH[CH_3 - (CH_2)_{16} - COOH]$, as glyceryl stearate or stearin, occurs in vegetable and animal fats, particularly in tallow. Stearic acid is only slightly soluble in alcohol or in ether. Its melting-point is 69.3° C.

Acrylic Acid Series.

Acrylic acid, $CH_2 : CH.COOH$, is a type of the double-bonded acids. It is a liquid with boiling-point at 140° C. Nascent hydrogen breaks the double bond, forming propionic acid, $CH_3.CH_2.COOH$. Hydriodic acid will also break the double bond by direct union of its constituents, forming $CH_2I - CH_2 - COOH$, (β-iodo propionic acid).

Acrylic aldehyde, or acrolein, is a colorless liquid boiling at 52° C. Its vapor has an irritating, pungent odor, sufficiently characteristic to be used as a qualitative test for glycerol, from which it is obtained by heating with $KHSO_4$.

The only other acid of particular interest in this series is oleic acid, $C_{17}H_{33}COOH$. It is an important constituent of oils, both animal and vegetable.

Its glyceryl ester, $C_3H_5(C_{17}H_{33}CO_2)_3$, forms a large part of lard oil, cotton-seed oil, or any oil obtained by cold expression.

Dibasic Acids.

$$
\begin{array}{lll}
\text{COOH} & \text{COOH} & \text{COOH} \\
| & | & | \\
\text{COOH} & \text{CH}_2 & \text{CH}_2 \\
\text{Oxalic acid.} & | & | \\
 & \text{COOH} & \text{CH}_2 \\
 & \text{Malonic acid.} & | \\
 & & \text{COOH} \\
 & & \text{Succinic acid.}
\end{array}
$$
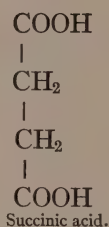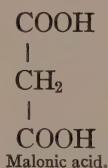
Dibasic acids contain two carboxyl groups. These are referable to, and in many cases may be formed from, the diatomic alcohols. Thus glycol, $\begin{array}{c}\text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH}\end{array}$, upon oxidation yields glycollic acid, $\begin{array}{c}\text{CH}_2\text{OH} \\ | \\ \text{COOH}\end{array}$, and oxalic acid, $\begin{array}{c}\text{COOH} \\ | \\ \text{COOH}\end{array}$.

Carbonic acid, $O = C \diagdown^{\text{OH}}_{\text{OH}}$, is dibasic in that it contains two atoms of replaceable hydrogen, though not two carboxyl groups. It is claimed that a molecule of this sort cannot exist because a single carbon atom cannot hold more than one hydroxyl group in combination. This acid has never been isolated, all attempts to separate it in the pure form resulting in the formation of carbonic acid gas and water. Its compounds (carbonates) are very common and very important, both in organic and inorganic chemistry. Organic salts of carbonic acid may be made by treating silver carbonate with alkyl iodide.

$$
CO\diagdown^{\text{OAg}}_{\text{OAg}} + 2\,C_2H_5I = CO\diagdown^{\text{OC}_2\text{H}_5}_{\text{OC}_2\text{H}_5} + 2\,AgI.
$$
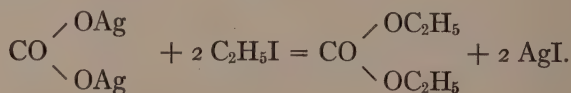
Oxalic Acid, which may be considered as a type of the dibasic acids, occurs as small, colorless crystals (four- or six-sided prisms), containing two molecules of water of crystallization

($H_2C_2O_4 \cdot 2 H_2O$); it is but slightly efflorescent, and, if carefully crystallized, is suitable for the preparation of standard acid solution. Salts of oxalic acid occur in many plants; the acid potassium oxalate, "salt of sorrel," is found in common red sorrel (Rumex acetora) and in wood sorrel (Oxalis acetocella). Oxalic acid in various combinations, often with lime, is widely distributed in articles of vegetable diet, particularly tomatoes, rhubarb, spinach, and asparagus; grapes, apples, and cabbages also carry oxalates but in smaller amounts.

The source of oxalates in the system is twofold, — the ingested oxalates and those produced by oxidation, incident to metabolism, the exact nature of which has not been clearly demonstrated (see Calcium and Sodium Oxalates, under Urine and Saliva).

Oxalic acid was previously made commercially by the action of strong nitric acid on starch or sugar; it is now prepared by heating cellulose (in form of sawdust) with a mixture of potassium hydroxide and sodium hydroxide, precipitating the acid as CaC_2O_4, and decomposing the salt by sulphuric acid. The acid is then purified by repeated crystallization.

Malonic Acid, $COOH-CH_2-COOH$, is an oxidation product of malic acid (from apples), and is comparatively unimportant.

Succinic Acid, $COOH(CH_2)_2-COOH$, occurs in amber, from which it takes its name (Amber-Succinum). It has been detected in the urine after asparagus and some fruits have been eaten. It occurs as colorless crystals, soluble in water, and only slightly soluble in ether. Succinic acid may be obtained by the saponification of ethylene cyanide, $C_2H_4(CN)_2$, and is a dibasic acid containing four carbon atoms. It is a constituent of some transudates and cyst fluids. It occurs in the spleen and thyroid gland, and has been found in sweat and in the urine (Hammarsten).

Pyro-tartaric Acid, formed by the distillation of ordinary tartaric acid, is one of four isomers of formula $C_5H_8O_4$, and is of

interest only in its relation to some of the amino acids which result from protein digestion.   Formula for pyro-tartaric acid is $CH_3 - CHCOOH - CH_2 - COOH$.

Oxyacids.

Hydroxy-acids, or alcohol acids, contain hydroxyl in place of one or more hydrogen atoms of the fatty acids.   Thus we may consider

Carbonic acid as hydroxyformic acid, $HO - COOH$;

Glycollic acid as hydroxyacetic acid, $\begin{matrix} CH_2OH \\ | \\ COOH \end{matrix}$;

Lactic acid as hydroxypropionic acid, $\begin{matrix} C_2H_4OH \\ | \\ COOH \end{matrix}$;

Malic acid (from apples) as hydroxy-
succinic acid, $\begin{matrix} CHOH - COOH \\ | \\ CH_2 - COOH \end{matrix}$

Tartaric acid as dihydroxysuccinic acid, $\begin{matrix} CHOH - COOH \\ | \\ CHOH - COOH \end{matrix}$

Citric Acid, from lemons, limes, etc., is in a class by itself. It is a tribasic acid (has three carboxyl groups and one hydroxyl); the formula is $C_3H_4OH - (COOH)_3$.

Glycollic Acid occurs in nature in unripe grapes, and possibly as antecedent to oxalates in the system (Dakin, Journal of Biol. Chem., 3.57).   Glycollic acid is formed from glycol by oxidation, and from glycocoll, by action of nitrous acid.

Nitric acid will oxidize glycollic acid to oxalic acid.

Lactic Acid. — Oxypropionic acid, or i *-ethylidene lactic acid, $CH_3 - CHOH - COOH$, is ordinary lactic acid produced by fermentation of milk-sugar, etc.   It occurs in the gastric juice

* Optically inactive.

and in contents of the intestine, "particularly during a diet rich in carbohydrates," possibly in muscle and brain tissue (Foster). It is not volatilized at temperatures below 160° C.

Sarcolactic or paralactic acid, d*-ethylidene lactic acid, occurs in meat extract. The presence of this acid causes the acid reaction of dead muscle, possibly of contracted muscle. It occurs in the blood and at times in the urine, and it is probable that it is this modification that may be found as lactates and acid lactates in the saliva and urine, the crystalline forms of which have been identified by Dr. E. C. Kirk of Philadelphia, by the use of the micropolariscopic method of Dr. Joseph P. Michaels of Paris.

The optical activity of the lactic acids depends upon the presence of an asymmetric carbon atom. This asymmetric carbon, as the name implies, is one holding four *different* groups or atoms as illustrated by the following compounds.

$$CH_3 \diagdown \diagup OH \qquad (C_2H_3O_3) \diagdown \diagup OH \qquad H \diagdown \diagup CH_2.COOH$$
$$C \qquad\qquad C \qquad\qquad C$$
$$H \diagup \diagdown COOH \qquad H \diagup \diagdown COOH \quad HO \diagup \diagdown COOH$$

Lactic Acid.   Tartaric Acid.   Malic Acid.
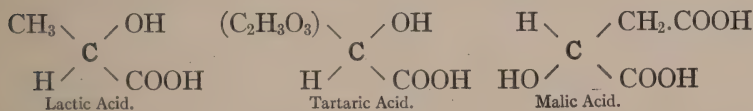
The truth of the above statement regarding the optical activity of these substances may be demonstrated quite readily by the reduction of the hydroxyl group in sarcolactic acid when the inactive propionic acid results.

$$CH_3 \diagdown \diagup OH \qquad\qquad CH_3 \diagdown \diagup H$$
$$C \qquad\qquad\qquad C$$
$$H \diagup \diagdown COOH \qquad\qquad H \diagup \diagdown COOH$$

Active.   Inactive.

The optical activity consists in the power of the substance to turn the ray of polarized light to the right or to the left.

Both of these acids form characteristic crystalline salts of zinc and of calcium. In cold water the zinc sarcolactate is

* Dextrorotary.

more soluble than zinc lactate; on the other hand, the calcium sarcolactate is rather less soluble than calcium lactate.

β-Oxybutyric Acid, $CH_3-CHOH-CH_2-COOH$.   If there is introduced into butyric acid, $CH_3-CH_2-CH_2-COOH$, an OH group, an oxybutyric acid results.   If this alcohol group (OH) occupies the secondary or β position (i.e., attached to the carbon atom twice removed from the carboxyl), the acid is the β-oxybutyric as above.

By oxidation of the compound, the alcohol group is broken up and hydrogen withdrawn to form water, leaving a keto acid, $CH_3-CO-CH_2-COOH$, known as diacetic acid.   This in turn may give off carbon dioxide and become dimethyl ketone, or acetone, $CH_3-CO-CH_3$.   These three substances, β-oxybutyric acid, diacetic acid, and acetone, are classed in von Noorden's " Autointoxication," and in the works of other recent writers, as " the acetone bodies," and by this convenient term we may refer to them collectively.   They occur in diabetic urine and, according to von Noorden, in other cases of perverted oxidation (not insufficient oxidation).

Tartaric Acid is a dihydroxysuccinic acid, $COOH-(CHOH)_2$ $-COOH$, obtained from grape-juice.

We see by an examination of the graphic formula of this acid that it contains two asymmetric carbon atoms.

$$
\begin{array}{c}
COOH \\
| \\
H-C-OH \\
| \\
OH-C-H \\
| \\
COOH
\end{array}
$$
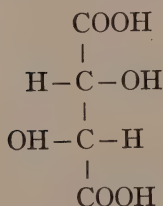
By placing the hydrogen or the hydroxyl on similar or opposite sides of the chain we see how it might be possible to obtain a new form of isomerism depending on the relative position of the atoms in space and not at all upon their attachment to other atoms of the molecule.   This is found to be the fact and this sort of isomerism resulting only in differing physical properties such as optical activity has been called physical isomerism or stereo-isomerism.

A mixture of equal weights of these two kinds of tartaric

acid crystallized together give an example of what is known as *di-* forms or racemic compounds.

The double tartrate of sodium and potassium (Rochelle salt), $KNaC_4H_4O_6$, is much used in medicine.

Tartaric acid combines with potassium and antimony to form tartar emetic, $(KSbOC_4H_4O_6)_2$, H_2O.

The " *scale salts of iron*," " ferri et ammonii tartras " and " ferri et potassii tartras," are prepared by dissolving freshly precipitated ferric hydroxide, in the acid tartrate of ammonia or potash, and, after evaporation to thick syrup, solidifying in thin layers on glass plates.

Potassium Bitartrate, or acid tartrate, $KHC_4H_4O_6$, is cream of tartar, and one of the few salts of potassium only sparingly soluble in water. Its commercial source is the wine-vat.

Monobasic Amino Acids.

Amino acids, formerly called amido acids, are characterized by an NH_2 group in place of hydrogen; for example, acetic acid is

$$\begin{array}{c} CH_3 \\ | \\ COOH \end{array} \qquad \text{Amino acetic acid is} \qquad \begin{array}{c} CH_2NH_2 \\ | \\ COOH \end{array} \qquad \text{These acids are of}$$
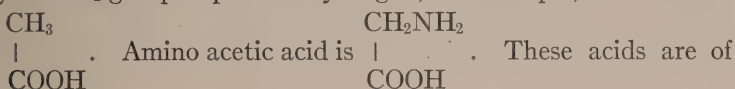
particular interest because of their close relationship to protein, many of them being among the cleavage products of protein hydrolysis.

That many of the amino acids are formed as intermediate steps in the reduction of the complex protein molecules to urea is certain.

A faulty metabolism, which stops short of normal oxidations, results in throwing these amino acids off in the urine or feces and their presence indicates abnormal conditions of one sort or another.

$$\text{Amino formic or carbamic acid,} \quad \begin{array}{c} NH_2 \\ | \\ COOH \end{array} \quad \text{, is a hypothetical}$$
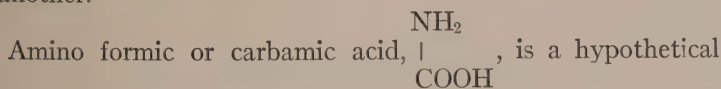
acid which would consist simply of an amino group, NH_2, united to a carboxyl group, COOH. By the union of ammonia and carbon dioxide the ammonium salt of this acid is formed,

$$2 NH_3 + CO_2 = \begin{array}{l} NH_2 \\ | \\ COONH_4 \end{array}$$
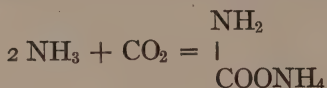
Ammonium carbamate is a constituent of commercial ammonium carbonate and an antecedent of ammonium carbonate in the hydrolysis of urea.

Amino-acetic Acid, also called glycocoll and glycin, is obtained with other amino acids by boiling glue with either acids or alkalies.* It is also obtained, by the hydrolysis of glycocholic acid, from bile.

Hippuric Acid (Plate V, Fig. 4) consists of benzoic acid united chemically to glycocoll, and may be produced synthetically by the union of these two substances.

Amino-Valeric Acid, $CH_2(NH_2) - (CH)_3 - C_2OOH$, may be obtained with glycocoll from elastin, the protein of the elastic fibers, of tendons, etc.† Isomeric with **amino-caproic acid** is *leucin,* an amino-isobutyl-acetic acid.

$$\begin{array}{l} CH_3 \\ \diagdown \\   CH - CH_2 - CH(NH_2) - COOH. \\ CH_3 \diagup \end{array}$$
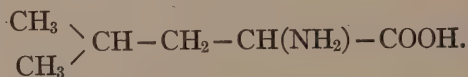
Leucin, $(CH_3)_2CH.CH_2.CHNH_2.COOH$, is an α-amino-isobutyl-acetic acid and occurs, usually with tryosin, as a decomposition product of the proteins, including keratin and collagen. It results from the tryptic digestion of the hemipeptones and is regarded with other amino acids as among the antecedents of urea. Leucin only rarely occurs in the urine. When pure it crystallizes in thin, hexagonal plates, but as found in urine it is usually in the form of " spheres " represented by Fig. 2 of Plate V.

* Bernthsen, Organic Chemistry.
† Foster, Chemical Basis of the Animal Body.

Cystin, $C_6H_{12}N_2S_2O_4$, is an amino acid occasionally found in the urine in diseases where the sulphur compounds fail to be properly oxidized. It occurs under these circumstances as regular colorless hexagonal plates (Plate X, Fig. 6).

By the oxidation of cystin and subsequent splitting off of carbon dioxide taurine is produced. For occurrence of taurine see page 232.

Tyrosin is a complex amino acid obtained from the decomposition of protein substances, particularly old cheese. It is occasionally found in urinary sediments as colorless needle-shaped crystals usually grouped as tufts or "sheaves" (Plate V, Fig. 6).

DIBASIC AMINO ACIDS.

Of this class of compounds two may be mentioned: aminosuccinic, aspartic or asparaginic acid, $COOH - CH_2 - CH(NH_2) - COOH$, may be obtained from animal and vegetable proteins and in the pancreatic digestion of fibrin.

Glutamic Acid is an amino-glutaric (pyrotartaric) acid, and occurs similarly to aspartic acid, except that it is not formed by pancreatic digestion.

CHAPTER XXV.

CYANOGEN COMPOUNDS. SULPHUR COMPOUNDS.

CYANOGEN, C_2N_2, is an intensely poisonous gas, colorless, heavy (specific gravity 1.81), and inflammable. It is very easily soluble in water or alcohol, forming unstable solutions, which, upon decomposition, give rise to various nitrogen compounds, among them ammonia, hydrocyanic acid, and urea.

Cyanogen may be prepared by heating the cyanides of silver, mercury, or gold, or by the dry distillation of ammonium oxalate.

Hydrocyanic Acid, HCN, may be produced by the fermentation of the glucoside amygdalin from bitter almonds; also from the kernel of peach-stones, cherry-laurel leaves, etc. Hydrocyanic acid may be formed by direct synthesis of C_2H_2 (acetylene) and nitrogen. The synthesis is induced by passing electric sparks through the mixed gases. It is conveniently prepared in the laboratory by distilling a mixture of dilute sulphuric acid with potassium ferrocyanide, $K_4Fe(CN)_6 + 5\ H_2SO_4 = 6\ HCN + FeSO_4 + 4\ KHSO_4$. Hydrocyanic acid is a colorless, poisonous liquid, boiling at 26.5° C., with a characteristic odor often designated as a peach-stone odor. It is soluble in water and a two per cent. aqueous solution constitutes the acidum hydrocyanicum dilutum of the pharmacopœia, also known as prussic acid.

Potassium Cyanide (KCN or KCy) occurs in trade as a white solid, sometimes granular, more often as a powder. It is intensely poisonous owing to the dissociation of the salt and activity of the free cyanogen.

Potassium cyanide is decomposed by carbonic acid of the air with liberation of hydrocyanic acid. The aqueous solution of potassium cyanide hydrolyzes in two distinct ways: the most easily apparent at ordinary temperature is with the formation of hydrocyanic acid and potassium hydroxide giving the solution an alkaline reaction:

$$KCN + H_2O = HCN + KOH.$$

Upon boiling a solution, the second hydrolysis may be demonstrated whereby ammonia and potassium formate are produced:

$$KCN + 2 H_2O = HCOOK + NH_3 \text{ (Exp. 119)}.$$

The organic cyanides are known as *nitrils* or *isonitrils*, according as the hydrocarbon radical is attached directly to the carbon or to the nitrogen of the cyanogen group. That is, methyl cyanide would be represented by CH_3-CN, while the isocyanide would be CH_3-NC (methyl carbamine); the nitrogen atom being in the first place trivalent, in the second quinquivalent.

Of these two classes of compounds, the isocyanides are of much greater interest to the student of dental medicine owing to their relation to the isocyanates and to urea.

Phenyl-isocyanide, C_6H_5NC, also known as isobenzonitril, is produced by warming aniline ($C_6H_5NH_2$) with alcoholic potash and chloroform, the intensely disagreeable odor of which is utilized as a test for chloroform or chloral hydrate (page 176); or, with chloroform and potassium hydrate, the production of this isocyanide may become a test for aniline, acetanilide (antifebrin), and other derivatives of aniline.

Potassium Ferrocyanide, yellow prussiate of potassium, $K_4Fe(CN)_6$, is obtained by heating animal refuse with a little over one-third its weight of potassium carbonate and scrap iron. The mixture is covered so as to exclude the air and after cooling the resulting mass is boiled with water and filtered.

Upon evaporation of the filtrate potassium ferrocyanide will separate as yellow, four-sided crystals with a formula $K_4Fe(CN)_6$. $3 H_2O$. The complex acid ion $(Fe(CN)_6)$ is not regarded as poisonous but can be made to dissociate by the addition of acid. See Exp. 122. By the action of strong sulphuric acid the radical is broken up and carbon monoxide is evolved. Dilute sulphuric acid will yield hydrocyanic acid according to the reaction on page 228.

Potassium Ferricyanide, red prussiate of potassium, $K_3Fe(CN)_6$, contains iron in the ferric condition and may be made by oxidizing the ferrocyanide by the action of chlorine gas.

Cyanic Acid, HCNO, may be made by distillation of its polymer, cyanuric acid $(HCNO)_3$. Cyanic acid cannot be made in the usual way by decomposition of its salts with mineral acids, since in the presence of water cyanic acid becomes ammonium carbonate.

Potassium cyanate may be prepared by direct oxidation of potassium cyanide with lead oxide.

Ammonium cyanate passes, upon heating, directly into urea. See Exp. 126.

Isocyanic Acid, $O = C = N–H$ (carbimide) is supposed to be the acid of ordinary potassium and ammonium cyanates.

Fulminic acid $(C \equiv N–O–H)$, isomeric with cyanic acid $N \equiv C–O–H$ and isocyanic acid $(O = C = N–H)$, is important only because of its relation to the fulminates, which are explosive compounds of the acid, with some of the heavy metals, such as silver and mercury.

Thiocyanic Acid or Sulphocyanic Acid. — In this acid and its salts, the atom of sulphur replaces the oxygen of cyanic acid in the empirical symbol (HCNS); but, graphically, the sulphur is attached to the basic element (metal or hydrogen) rather than to carbon: thus, $K–S–C \equiv N$, that is, the sulphocyanate is not an isocompound. For occurrence and relations of HCNS in the human body, see chapter on Saliva.

Sulphur Compounds.

Mercaptan, an organic sulphhydrate. The name mercaptan comes from two Latin words signifying "taking mercury" (mercurium captans), because of compounds readily formed with mercuric oxide. Representatives of this class of compounds are found as derivatives of both the open and the closed-chain hydrocarbons.

Ethyl mercaptan, thioalcohol, C_2H_5SH, is a type of this class. It is a colorless liquid, with bad odor, slightly soluble in water, boils at 37° C., and is used in the preparation of sulphonal.

The mercaptans may be prepared by action of KHS on the alkyl haloids:

$$C_2H_5I + KHS = C_2H_5SH + KI.$$

The thioalcohols form potassium and sodium compounds similar to common alcohol,

$$C_2H_5SH + K = C_2H_5SK + H.$$

Mercaptol, a name which has been applied to the thioketones. The simple compounds of this class are not known as they form polymers very readily. A dimethyl-diethyl compound is produced in the process for preparation of sulphonal.

Thioethers are organic sulphides prepared in a manner analogous to that employed in the preparation of the thio-alcohols, the inorganic sulphide being used in place of the sulphhydrate, for example: $2 C_2H_5Br + K_2S = (C_2H_5)_2 S + 2 KBr.$

Sulphones are oxidation products of organic sulphides: as, for example, ethyl sulphone $\begin{array}{c} C_2H_5 \\ C_2H_5 \end{array}\!\!\diagdown\!\!S\!\!\diagup\!\!\begin{array}{c} O \\ O \end{array}$.
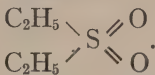
Sulphonal is a derivative of mercaptan as previously stated. It may be prepared by the action of acetone and ethyl mercaptan with hydrochloric acid and subsequent oxidation of the resulting product.

Sulphonic Acids as a class may be obtained by the oxidation of an organic sulphhydrate (mercaptan). This oxidation may be produced by the action of nitric acid or potassium permanganate, and may be written as follows:

$$C_2H_5SH + 3\,O = C_2H_5.SO_2.HO.$$
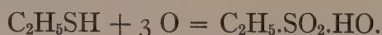
Taurine is an important sulphonic acid of the paraffin series. Its graphic formula shows it to be an amino ethyl sulphonic acid, $C_2H_4\!\!\begin{smallmatrix}\diagup\,HSO_3\\ \diagdown\,NH_2\end{smallmatrix}$. Taurine is derived from taurocholic acid by hydrolysis. This acid is representative of one of the two principal acid groups occurring in the bile, the salts of which may be found in pathologic conditions in the urine, or, according to Dr. J. P. Michaels and others, in the saliva.

CHAPTER XXVI.

AMINES OR SUBSTITUTED AMMONIAS.

IF one or more of the hydrogen atoms of ammonia, NH_3, be replaced by a hydrocarbon group, the resulting compound is an amine; thus CH_3-NH_2 is methylamine, and $(CH_3)_2NH$ is dimethylamine. Trimethylamine, $(CH_3)_3N$, has been found among the decomposition products of fresh brain, human liver, and spleen.*

When one hydrogen atom only has been substituted in NH_3 the amine is known as a primary amine or amino compound (containing the NH_2 group). These may be prepared in a number of ways, two of which we will consider.

If alkyl iodides or bromides are heated with alcoholic ammonia, compounds are produced analogous in composition to the ordinary ammonium salts:

$$CH_3I + NH_3 = NH_2CH_3.HI.$$

Upon distilling the methyl ammonium iodide (of this reaction) with caustic alkali the amine results:

$$NH_2CH_3HI + KOH = NH_2CH_3 + KI + H_2O.$$
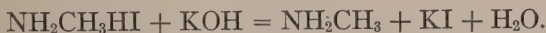
The second method is by the action of nascent hydrogen upon alcoholic solution of the nitrils:

$$CH_3CN + 2 H_2 = C_2H_5NH_2.$$

The disagreeable odor of carbylamine constitutes a characteristic test for the primary amines. This is known as Hofmann's Carbylamine Reaction and may be easily brought about

* Vaughn and Novy, Cellular Toxins.

by warming the amine with a little chloroform and alcoholic potash.

The secondary amines are those in which two hydrogen atoms of ammonia have been replaced as in dimethyl amine $(CH_3)_2NH$. These compounds have also been called imines (imides) or imino (imido) compounds because they contain the "imino" group (NH).

Imides are formed with a number of the dibasic organic acids. The one of greatest interest is perhaps the imide of succinic acid which may be produced by the following reaction. Ammonium succinate subjected to heat splits off $2 H_2O + NH_3$,

becoming $\begin{array}{l} CH_2.CO \\ | \quad\quad\quad NH. \\ CH_2.CO \end{array}$ The hydrogen of the imide group

may be replaced by metals such as potassium, silver, or mercury. Succinimide may also be produced by heating succinic acid, carbonic anhydride, and ammonia. This with mercuric oxide will give a white powder soluble in water, which is the mercuric succinimide largely used for the treatment of pyorrhea.

The secondary amines may be produced by further action of alkyl iodides and the primary amines. By action of sodium nitrite and hydrochloric acid upon fairly strong solution of a secondary amine a nitrosamine is formed which, when mixed with phenol and strong sulphuric acid, gives a dark green solution which becomes red upon dilution with water and this in turn becomes blue or green upon neutralization with a fixed alkali.

Trimethyl amine formed with the methyl and dimethyl amines is a liquid with a not unpleasant odor.

Diamines are derived from two molecules of ammonia, as ethylene diamine, $C_2H_4\begin{array}{l} \diagup NH_2 \\ \diagdown NH_2 \end{array}$.

To this class of compounds belong many of the "ptomaines," produced by the putrefaction of organic matter, as putrescine (butylene diamine), $CH_2NH_2 - (CH_2)_2 - CH_2NH_2$, and cadaver-

ine (penta-methylene diamine), $CH_2NH_2 - (CH_2)_3 - CH_2NH_2$. A large number of the ptomaines are aromatic compounds and as such will be referred to later.

AMIDES.

If the hydrogen of ammonia be replaced by an oxygenated or acid radical, an amide results; thus $NH_2(C_2H_3O)$ is acetamide, or this compound may be regarded as acetic acid, $CH_3 - COOH$, in which the OH has been replaced by NH_2.

It may be easier for the student to remember an amide as an organic acid with the OH of its carboxyl replaced by the "amido" or amino group NH_2.

Acetamide may be prepared by the action of strong ammonia upon ethyl acetate:

$$CH_3COOC_2H_5 + NH_3 = CH_3CONH_2 + C_2H_5OH.$$

It forms colorless crystals soluble in both alcohol and water.

Cyanamide (NH_2 in place of the hydroxyl of cyanic acid), $NCNH_2$, is prepared by the action of ammonia on cyanogen chloride. The calcium compound is of commercial importance as a means of utilizing atmospheric nitrogen for agricultural purposes. CaC_2 heated with N_2 becomes $NCNCa$; this in a crude state is used as fertilizer. The calcium cyanamide by action of carbon dioxide, water, and soil bacteria becomes first urea, then ammonium carbonate. See page 237.

Formamide, $CHO.NH_2$, is a liquid miscible with both alcohol and water. It boils with partial decomposition at about 200° C. Upon heating quickly, it splits into carbon monoxide and ammonia. (Bernthsen.)

Phenyl-formamide, $CHO.NHC_6H_5$, known as formanilide, occurs as yellow crystals soluble in water and in alcohol.

HYDRAZINES.

From diamide, $NH_2 - NH_2$, or hydrazine, may be derived such substitution products as methyl-hydrazine, $CH_3 - NH - NH_2$;

ethyl-hydrazine, $C_2H_5-NH-NH_2$;   and   phenyl-hydrazine, $C_6H_5NH-NH_2$.

This latter compound forms, with the monosaccharids and with many of the disaccharids, yellow crystalline compounds, known as osazones, which are precipitated in characteristic crystalline forms, recognizable upon microscopical examination and by their melting-points (see under Carbohydrates, page 261).

CHAPTER XXVII.

UREA AND URIC ACID.

THIS substance forms about 50% of the total solids and about 85% of the nitrogenous matter contained in the urine. When we consider that only 5% of the nitrogenous waste passes off in the feces and 95% in the urine, the importance of urea as an index of the nitrogen excreted and of protein metabolism becomes apparent.

Urea was the first organic substance synthesized from inorganic compounds. This was accomplished by producing a molecular rearrangement of ammonium isocyanate. The reaction is conveniently brought about by the double decomposition of potassium cyanate and ammonium sulphate and subsequent evaporation of the solution to dryness:

$$2\,CNOK + (NH_4)_2SO_4 = 2\,OCN.NH_4 + K_2SO_4.$$

Then $O = C = N - NH_4$ (ammonium isocyanate) $+$ heat $=$

$$O = C \begin{smallmatrix} \diagup NH_2 \\ \diagdown NH_2 \end{smallmatrix} \text{ (urea).}$$
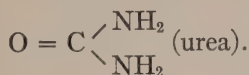
Urea is the amide of carbonic acid, $O = C \begin{smallmatrix} \diagup OH \\ \diagdown OH \end{smallmatrix}$, and from this type may be explained the rapid transformation of urea into ammonium carbonate in stale urine. $O = C \begin{smallmatrix} \diagup NH_2 \\ \diagdown NH_2 \end{smallmatrix}$ with one molecule of H_2O becomes $O = C \begin{smallmatrix} \diagup ONH_4 \\ \diagdown NH_2 \end{smallmatrix}$ or ammonium carbamate, and this, by addition of a second molecule of water, be-

comes $O = C\begin{cases} ONH_4 \\ ONH_4 \end{cases}$ or ammonium carbonate, $(NH_4)_2CO_3$.
The last part of the reaction takes place whenever commercial
"ammonium carbonate" [really a mixture of carbamate
$(NH_4-NH_2-CO_2)$ and acid carbonate (NH_4HCO_3)] is dissolved
in water.

Urea crystallizes in long needle-shaped crystals of the rhom-
bic system. It is insoluble in water, somewhat soluble in
alcohol, and nearly insoluble in ether. It fuses at $132°$, and at
a somewhat higher temperature it gives off ammonia and am-
monium carbonate, and at $160°$ leaves a residue of ammelide,
cyanuric acid, and biuret. Urea is decomposed by solutions of
the alkaline hypochlorites or hypobromites, being broken up into
N, CO_2, and H_2O, as follows:

$$CO(NH_2)_2 + 3\ NaOBr = CO_2 + N_2 + 2\ H_2O + 3\ NaBr.$$

Cyanuric Acid, $N_3C_3O_3H_3$, is a polymer of cyanic acid
(NCOH), which is, at first, formed in the above decomposition.

Biuret, $H-N\begin{cases} CO-NH_2 \\ CO-NH_2 \end{cases}$, may be obtained by heating
urea. When pure, it occurs as white, needle-shaped crystals.
With NaOH and 1% $CuSO_4$ it gives the characteristic violet and
rose-red shades obtained in the biuret reaction (Piotrowski's
protein test). Exp. 189, page 406.

Urea Nitrate may be precipitated from fairly concentrated
urine by addition of HNO_3. It separates in hexagonal crystals
or plates, easily recognizable under the microscope (Plate V,
Fig. 3, opposite page 204).

Urea Oxalate. — Upon addition of a solution of oxalic acid
to concentrated urine, crystals of oxalate of urea are precipi-
tated. They are rather more easily obtained in characteristic
forms (Plate II, Fig. 5, opposite page 170) than are the crystals
of nitrate, and, in consequence, treatment with oxalic acid con-
stitutes a better method for the qualitative detection of urea in

the body fluids than the nitric acid test formerly used. These crystals polarize light, and the use of the micropolariscope facilitates their detection.

Substituted Ureas. — The hydrogen of the amino group may be replaced by alcohol radicals forming what are known as alkylated ureas; thus, $O = C \diagup{}^{NH_2}_{\diagdown NHCH_3}$ is methyl urea, $O = C \diagup{}^{NH_2}_{\diagdown NHC_2H_5}$, ethyl urea, and one, two, three, or all four of the hydrogen atoms may be so replaced.

When, in place of an alcohol radical, the *acid* radical is introduced, a class of compounds known as "ureides" results; thus

$$O = C \diagup{}^{NH_2}_{\diagdown NH(C_2H_3O)} \text{ (acetyl urea).}$$
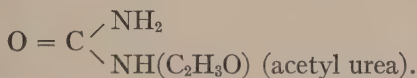
In a case of a dibasic acid, such as oxalic, $\begin{array}{c} COOH \\ | \\ COOH \end{array}$, entering into the reaction, one or both (OH) groups may be split off, forming in the first instance a ureide acid, as $O = C \diagup{}^{NH_2}_{\diagdown NH.CO.COOH}$, oxaluric acid,

$$\begin{array}{c} COOH \\ | \\ COOH \end{array} + O = C \diagup{}^{NH_2}_{\diagdown NH_2} = O = C \diagup{}^{NH_2}_{\diagdown NH - CO} + H_2O,$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad | $$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad COOH$$
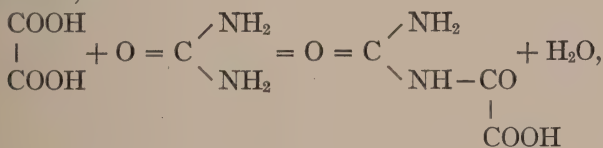
or, in the second case, a ureide, as $O = C \diagup{}^{NH-C=O}_{\diagdown NH-C=O}$ parabanic acid.

If the residue of *two* molecules of urea enter into the composition of the new molecule, the compound is a diureide. Of this class one of the most important is:

Uric Acid, trioxypurin, $C_5H_4N_4O_3$. Its relation to urea may

be shown by the graphic formula

$$\begin{array}{ccc} & NH-CO & \\ & | \quad | & \\ O=C & C-NH\diagdown & \\ & | \quad \| & C=O. \\ & NH-C-NH\diagup & \end{array}$$
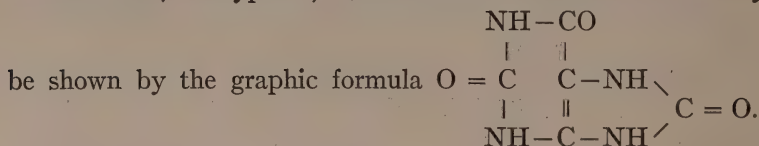
Uric acid is also referable to a purely hypothetical base, "purin," by the use of which the relationship of xanthin, hypoxanthin, and other "purin" or nuclein bases is easily demonstrated.

These bases are of great physiological interest, in that they form an unquestioned link between the decomposition products of the proteins, nuclein, etc., on the one hand, and uric acid and the urates on the other.

Uric acid normally occurs in the urine combined with alkaline bases, also with traces of calcium and magnesium. It is insoluble in alcohol, ether, or dilute acids; practically insoluble in water, but much more soluble in solutions of urea or of glycerin. A solution of uric acid does not redden blue litmus.

Purin is represented by the formula $C_5H_4N_4$, or graphically

as

$$\begin{array}{ccc} N=C-H & \\ | \quad | & \\ H-C \quad C-N-H & . \\ \| \quad \| \quad \diagdown C-H \\ N-C-N\diagup \end{array}$$
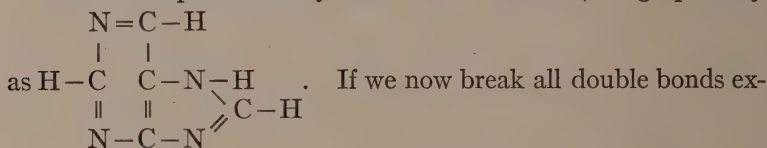
If we now break all double bonds except those linking two carbon atoms (4 and 5), we obtain a

graphic nucleus,

$$\begin{array}{ccc} 1-N-C^6 & \\ | \quad | & \\ 2=C \quad C^5-N-7 & \\ | \quad \| \quad \diagdown C=8 \\ 3-N-C^4-N-9 \end{array}$$

, by numbering the atoms
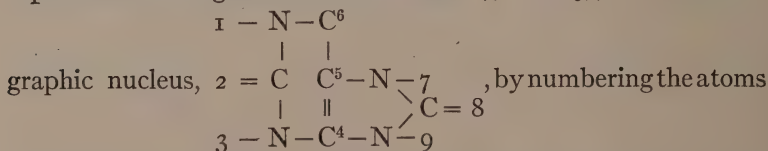
of which we may easily designate any structural formula of the group; thus, $2-6-8$, trioxypurin, is uric acid as above, while

xanthin is $2-6$, dioxypurin,

$$\begin{array}{ccc} H-N-C=O & \\ | \quad | & \\ O=C \quad C-N-H & \\ | \quad \| \quad \diagdown C-H \\ H-N-C-N\diagup \end{array}$$

, and $1-3-7$,
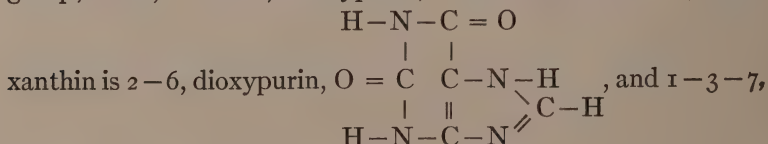
$$CH_3 - N - C = O$$

trimethyl-xanthin, $O = C \quad C - N - CH_3$, is caffein and thein,

$$CH_3 - N - C - N$$

alkaloids from coffee and tea.

Traces of xanthin (2.6 dioxypurin), hypoxanthin (6 oxypurin), guanin (2 imino, 6 oxypurin), adenin (6 amino purin), and heteroxanthin (7 methyl xanthin) have been found in urine, and, in cases of leukemia, many of them in increased amounts, notably xanthin, hypoxanthin, and adenin (Witthaus).

Uric acid occurs in the urine; there are traces of it in the blood; and it is occasionally found, in the form of urates, in saliva. It is a dibasic crystalline acid, colorless when pure; but, in urinary sediment, it occurs generally as crystals, yellow to red, "whetstone"-shaped, and in various other forms (Plate X, Figs. 1 and 2). The "brickdust" deposit occasionally found in urine consists of uric acid. It is insoluble in alcohol and nearly insoluble in water; but its solubility in water is increased by the presence of urea.

Upon heating uric acid, urea and cyanuric acid may be obtained; NH_3 and CO_2 are given off. We are not to infer from this decomposition that the uric acid is an antecedent of urea in the animal body; for such is not the case, except possibly to a limited extent.

Uric acid produces, upon oxidation, a variety of compounds, according to the temperature and the oxidizing agent employed.

Chlorine, hot, yields cyanuric acid, $C_3N_3(OH)_3$. Chlorine or bromine, cold, forms oxalic acid, alloxan $\left(CO\begin{smallmatrix} \nearrow NHCO \searrow \\ \searrow NHCO \nearrow \end{smallmatrix} CO \right)$,

parabanic acid $\left(CO\begin{smallmatrix} \nearrow NH-CO \\ \quad | \\ \searrow NH-CO \end{smallmatrix} \right)$ and ammonium cyanate.

HNO_3 in the cold, forms alloxan, alloxantin, and urea (Witthaus).

Uric acid may be detected by the murexide* test.   See **Exp.
131**, page 394.

While uric acid is practically insoluble in H_2O and the acid
urates only sparingly soluble, the uric acid in the system is
apparently held in solution as an acid urate $(Na\overline{HU})$ by the
presence of the sodium phosphates, NaH_2PO_4 and Na_2HPO_4,
possibly also aided by the presence of some unknown organic
combination.

$Na\overline{HU} + NaH_2PO_4$ forms, at 38° C., a solution with an acid
reaction; if, however, the mixture is cooled to room tempera-
ture, the reaction becomes alkaline from Na_2HPO_4, and uric
acid is precipitated (Bunge):

$$Na\overline{HU} + NaH_2PO_4 = Na_2HPO_4 + H_2\overline{U}.$$
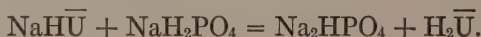
Na_2HPO_4 is a normal constituent of the blood, and a tendency
to precipitate uric acid may be met by the following reac-
tion: $Na_2HPO_4 + H_2\overline{U} = NaH_2PO_4 + Na\overline{HU}.$ Because the acid
urate of lithium is much more soluble in water than any of the
other monometallic urates, lithium salts have long been used as
uric acid solvents.   But the fact that lithium solutions will
precipitate from solutions of Na_2HPO_4 crystals of Li_2HPO_4, has
been made the basis for a claim that such use of lithium salts is
without effect other than to decompose and render insoluble
the alkaline phosphate, which has been acknowledged a valu-
able factor in keeping uric acid in solution.   While the disodic
phosphate is regarded by many as superior to lithium salts as
a uric acid solvent, the fact of comparative insolubility of
Li_2HPO_4 can hardly be regarded as conclusive evidence that
lithium compounds are not effective.

The following in regard to our need for "sarsaparilla" in
the spring is given by Dr. E. C. Hill, of the University of Den-
ver, in his text-book of chemistry, page 370: "Reduced alka-

---

* *Note.* — Murexide is a definite chemical compound $(C_8H_5N_5O_6)$ and may be
produced from alloxantin, an oxidation product noted above.

linity of the blood, as in winter from eating meats freely, throws uric acid out of solution to collect in the more acid tissues (spleen, liver, and joints).   With the vernal tide of alkalinity (due to freer sweating, with excretion of fatty acids) these deposits are swept out in the blood-current, irritating the nerves and giving rise to 'that tired feeling.'"

CHAPTER XXVIII.

CLOSED-CHAIN HYDROCARBONS.

IN illustrating the simpler relationship of organic compounds we have, as far as possible, carefully avoided reference to the closed-chain or aromatic compounds, as the characteristic groupings are more easily seen by the use of simple formulæ. The distinguishing feature of the aromatic (also called cyclic) compounds is a nucleus consisting of a closed chain of atoms; this chain may contain three, four, five, six, or seven members, but the six-carbon ring is by far the most important, and the only one which we are to consider.

The hydrocarbons of the aromatic series have, for a general formula, C_nH_{2n-6}, the simplest being *benzene* or benzol, C_6H_6; and we may consider that the aromatic compounds are derived from this. The structure of the benzene molecule is represented by Kekulé's benzene ring. Note that there are three double bonds, which of course permit of addition products, as $C_6H_6Cl_2$, benzene di-chloride, etc. The substitution products are, however, of far greater importance.

Benzene, C_6H_6 (benzol), is a colorless liquid from the "light-oil" obtained by distillation of coal-tar. It boils at 80°, has a gravity of 0.899, is soluble in ether, alcohol, and chloroform, but insoluble in water. It may be made pure by distilling an intimate mixture of benzoic acid and quicklime, and at a temperature of about 5° C. may be obtained as a crystalline solid, $C_6H_5COOH + CaO = CaCO_3 + C_6H_6$. (See Exp. 135, page 395.)
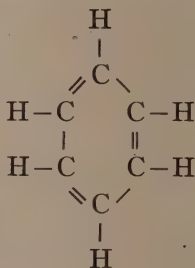
Benzene may be considered as phenyl hydride, C_6H_5H, and similarly to the straight chain hydrocarbons two of these phenyl groups may be made to combine giving a hydrocarbon $C_{12}H_{10}$, known as diphenyl. Reaction $2 C_6H_5Br + 2 Na = C_{12}H_{10} + 2 NaBr$.

Toluene, (toluol). — The next higher homologue of the series will be C_7H_8; this is methyl benzene ($C_6H_5CH_3$) or toluene.

The hydrocarbons of this series may be prepared in a manner similar to that used in the preparation of the hydrocarbons of the paraffin series.

Toluene may be made by the action of metallic sodium upon a mixture of brombenzene and methyl iodide.

$$C_6H_5Br + CH_3I + Na_2 = C_6H_5CH_3 + NaBr + NaI.$$
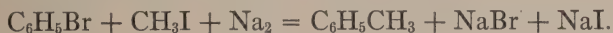
Toluene is a colorless liquid boiling at 110° C., and yielding upon oxidation a benzene derivative; i.e., the CH_3, or so-called side chain, is the part of the compound changed by oxidizing agents rather than the benzene ring,

$$C_6H_5CH_3 + 3 O = C_6H_5CO_2H + H_2O.$$
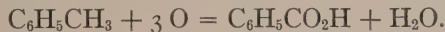
Xylene, C_8H_{10} (xylol) or dimethylbenzene, the next hydrocarbon of this series, exists in coal tar as a mixture of three isomeric compounds which may be graphically represented as follows:
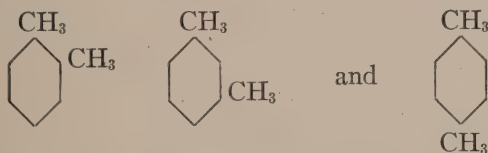
These three possible positions of the *second* substitution are known as ortho-, meta-, and para-; thus, the first representation at the left will be ortho-xylene, or ortho-dimethylbenzene. The other two will be meta-xylene and para-xylene respectively.

A trisubstituted benzene may be "adjacent," if the substituted element or group is attached to the carbon atoms

1—2—3, or "unsymmetrical" 1—2—4, or "symmetrical" 1—3—5.

A fourth isomer of dimethylbenzene would be an ethyl benzene, $C_6H_5C_2H_5$. This, upon oxidation, yields benzoic acid, in a manner similar to toluene. (Bernthsen.)

Mesitylene, C_9H_{12}, is a trimethylbenzene. Only two isomers are possible. It can be prepared by dehydrating acetone by the use of sulphuric acid:

$$3\ C_3H_6O - 3\ H_2O = C_9H_{12}.$$
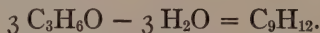
Hydroxy Derivatives of the Aromatic Hydrocarbons.

Phenol, carbolic acid, or oxybenzene, C_6C_5OH, obtained from the distillation of coal-tar, and used as an antiseptic and disinfectant. For properties and test, see page 183. Phenol acts like an acid, in that it forms salts with the metallic bases, C_6H_5OK, potassium phenolate, but it does not have an acid reaction on litmus paper or other indicators, i.e., it does not have free hydrogen ions when in solution, but belongs to the alcohols rather than the acids.

The three di-hydroxybenzenes are all of interest and are graphically represented as follows:

ortho-dihydroxy benzene or pyrocatechol

meta-dihydroxy benzene or resorcinol

and

para-dihydroxy benzene or hydroquinol
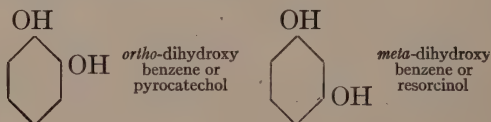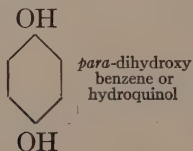
The ortho compound is **pyrocatechol.** Its ethereal sulphate (acid sulphate) is given by Hoppe-Seyler as a constituent of normal urine, and its monomethyl ether, **guaiacol,** $C_6H_4OH-O-CH_3$,

is obtained from beech-wood creosote, of which it constitutes the greater part (60 to 90 per cent U. S. D.). Guaiacol and various compounds produced from it have been widely recommended for tubercular diseases.

Pyrocatechol has been found to be the most practical reagent for the detection of oxidizing enzymes * in the saliva.

Resorcinol is a white crysta line solid, becoming more or less colored upon exposure to the light. It melts at 118° C., and, in solution, gives a purple color with ferric chloride. Heated with sodium nitrate, it produces a substance known as "Lacmoid" which is used to a considerable extent as an indicator.

The **hydroquinol,** or hydrochinon, is a white powder melting at 169° C., and is largely used as a photographic developer.

Pyrogallol, or trihydroxybenzene, $C_6H_3(OH)_3$ $(1-2-3)$, may be made by heating gallic acid, and because of this fact is usually called pyrogallic acid. It is a white silky crystal which, like hydroquinol, is used as a photographic developer. Dissolved in a solution of caustic potash it absorbs oxygen to a marked degree, and may be used as a reagent for the quantitative determination of oxygen in gas analysis.

Phloroglucinol is another trihydroxybenzene, isomeric with pyrogallol but with the hydroxyl groups occupying positions $1-3-5$ in the ring. The formula is $C_6H_3(OH)_3$ $(1-3-5)$.

It crystallizes in rhombic prisms, soluble in water, alcohol and ether. This is used in physiological chemistry as a reagent with vanillin as a test for free hydrochloric acid.

Thymol (3 methyl-6 isopropyl-phenol), $C_6H_3OH_{(1)}CH_{3(3)}C_3H_{7(6)}$, is a solid of the nature of camphor, melting at 44° C., and is obtained from various volatile oils, particularly from the oil obtained from Thymus Vulgaris. It is very sparingly soluble in water. The addition of a little alcohol increases the solubility. It is largely used in the preparation of antiseptic dental preparations, mouth washes, etc.

* Journal of the Allied Dental Societies, Vol. 4, page 346, Dec., 1909.

Cresol, $C_3H_4CH_3OH$, is a hydroxy-toluene. Three isomeric compounds of this formula are obtained from the distillation of coal tar between 200° and 210° C. The ortho and para cresols are solid at ordinary temperatures, the ortho compound melting at 31° C., the para at 36° C. Meta cresol is a liquid which does not solidify unless under extreme conditions of cold and pressure.

The cresols are similar to phenol not only in composition but also in physical and therapeutic properties; hence, cresol has been called cresylic acid, just as phenol has been called carbolic acid.

A mixture of the cresols, said to be composed of meta cresol 40%, ortho 35%, and para cresol 25%, constitutes the tricresol very largely used in dentistry as a germicide and antiseptic similar to carbolic acid.

An emulsion of cresol, obtained by the solution of resin soap as an emulsifying agent, is known as creolin. Cresol is also a constituent of the disinfectant lysol.

Tricresol is miscible with formalin in all proportions, and the mixture is recommended in the treatment of root canals.

Nitrogen Derivatives.

Benzidine, a diparadiamino derivative of diphenyl is made by the reduction of dinitrophenyl; is a solid substance melting at 122° C., and is used as a reagent in testing for blood.

Nitro-benzene, $C_6H_5NO_2$, may be produced by treating benzene with a mixture of nitric and sulphuric acid at reduced temperature. (Exp. 137, page 395.) It is a yellow, oily liquid, with the odor of bitter almonds, commercially known as oil of mirbane, and used in the manufacture of aniline.

Aniline or Amino-benzene, $C_6H_5NH_2$. By reaction of nitrobenzene with nascent hydrogen, the NO_2 group becomes an NH_2 group and aminobenzene or aniline is produced. Aniline, a colorless liquid, also called aniline oil, is important from a commercial rather than from a medical standpoint, as it forms the basis of

the aniline dyes. When pure it is a colorless liquid, but changes quite rapidly when exposed to the light. It is used in testing for chloral and chloroform. It is slightly soluble in water, and easily soluble in alcohol and ether. At 8° C. it becomes a crystalline solid.

Diphenylamine, $(C_6H_5)_2NH$, is formed by the substitution of the phenyl group for one of the amino hydrogens of aniline. It crystallizes from petroleum ether in white crystals which melt at 54° C.

Acetanilide, $C_6H_5.NH.COCH_3$, also known as antifebrine, may be produced by heating aniline and glacial acetic acid, crystallizes in colorless plates which melt at 115° C.

Amino-phenol may be formed by the reduction of nitrophenol by the action of nascent hydrogen (tin and hydrogen chloride). The para compound forms an ethyl ester which by action of glacial acetic acid gives phenacetine or para-acetphenetidine,

$$C_6H_4 \begin{cases} OC_2H_5. \\ NH.CO.CH_3 \end{cases}$$
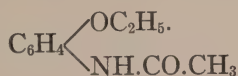
Picric Acid is trinitrophenol, $C_6H_2.OH.(NO_2)_3$. It may be formed by action of strong nitric acid, or mixture of sulphuric acid and nitric acid on phenol. It occurs as yellow plates slightly soluble in water, easily soluble in alcohol and ether, and is used in Esbach's reagent for the estimation of albumin in urine and as an alkaloidal precipitant.

Salvarsan, (606), arsenobenzol, more accurately paradiaminodioxyarsenobenzene hydrochloride, is an arsenic derivative of benzene used in medical practice as a specific for syphilis.

Aromatic Acids and Aldehydes.

Benzoic Acid, C_6H_5COOH, was originally produced from gum benzoin, but may be made from hippuric acid (q.v.), which (from urine of horses) formerly constituted a commercial source.

It is chiefly prepared, however, from toluene; it crystallizes in colorless plates or long prismatic crystals (from solution). It is sparingly soluble in cold water, more soluble in hot water, easily soluble in alcohol. It sublimes and is inflammable, burning without residue.

Benzoates of sodium, ammonium, lithium, and lime are all used in medicine. Benzoated or benzoinated lard is prepared by digesting gum benzoin in hot lard. This is much used as a base for ointments and keeps well.

Benzaldehyde, C_6H_5-CHO, is a colorless liquid, soluble in alcohol and ether, and sparingly soluble in water. The U. S. P. oil of bitter almonds is practically benzaldehyde; it is a volatile oil, very poisonous, and upon standing deposits benzoic acid from partial oxidation.

Salicylic Acid, orthohydroxybenzoic acid, $C_6H_4-OH.COOH$, is a white crystalline powder, odorless, irritating to mucous surfaces, soluble in alcohol and ether, and in about 450 parts of water at $15°$ C. (U. S. D.). Salicylic acid may be made by action of carbon dioxide on sodium phenate and subsequent decomposition of the sodium salicylate. By heating rapidly the acid may be changed into phenol and carbon dioxide.

Acetyl Salicylic Acid, $C_6H_4.C_2H_3O_2.COOH$, known in medicine as aspirin, may be obtained by heating salicylic acid with acetyl chloride. It occurs as white needles slightly soluble in water, soluble in alcohol and ether. Aspirin is decomposed in the intestine, salicylic acid appearing in the urine twenty to thirty minutes after administration of aspirin.

Salicylates have been used to considerable extent in various uric-acid diseases. Methyl salicylate constitutes 90% of natural oil of wintergreen (Gaultheria). The alcoholic solution is essence of checkerberry.

Salol is phenylsalicylate, $C_6H_4OH.COO(C_6H_5)$, a white crystalline powder, practically insoluble in water and not decomposed by the dilute acids of the stomach juices; but in the

intestine it becomes salicylic acid and phenol, as follows:

$$C_6H_4.OH.COOC_6H_5 + H_2O = C_6H_4OH.COOH + C_6H_5OH.$$
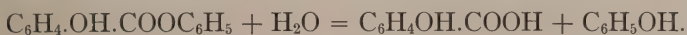
Gallic Acid, a trihydroxybenzoic acid, $C_6H_2(OH)_3COOH$, (1 : 2 : 3 : 5), is prepared from tannic acid by action of dilute sulphuric acid, or by oxidation by exposure of powdered galls. It forms slightly brownish crystals; if pure, the crystals are colorless. At ordinary temperatures one part of acid is soluble in about one hundred parts of water, five parts of alcohol or twelve parts of glycerine.

Tannic Acid, or Tannin, sometimes called di-gallic acid because its composition, $C_{14}H_{10}O_9$, corresponds to two molecules of gallic acid less one molecule of water, occurs in galls, in many astringent drugs and bark from various trees, as hemlock and oak. Tannic acid causes dark colored precipitate with ferric chloride, and precipitates gelatin, albumin and starch, differing in all of these particulars from gallic acid. (U. S. D.)

Hippuric Acid, benzoyl glycocoll, $C_6H_5\ CO.NH.CH_2 - COOH$, occurs in traces in human urine, to a considerable extent in the urine of the herbivora, but not at all in that of the carnivora. It crystallizes in prismatic needles (Plate V, Fig. 4), often resembling crystals of ammonium magnesium phosphate; but as these latter only occur in neutral or alkaline urine and hippuric acid, usually in acid urine, there is little danger of confounding the two substances. Hippuric acid is hydrolyzed by the urease of fermenting urine, forming benzoic acid and glycocoll (amino-acetic acid):

$$C_6H_5CO-NH-CH_2-COOH + H_2O$$
$$= C_6H_5COOH + CH_2NH_2COOH.$$
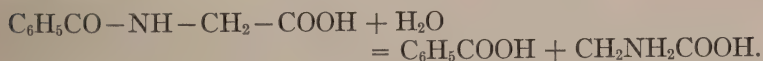
Tryosin, $C_6H_4OH - CH_2CH(NH_2) - COOH$, may be crystallized as fine silky needles. It is formed from protein substances, particularly casein and fibrin, both by the action of proteolytic enzymes and by putrefactive processes. It rarely occurs in urinary sediment; when found it is in bundles or sheaves (Plate V,

Fig. 6, page 204), and is usually indicative of acute liver disease, phosphorus poisoning, etc.

Phthalic Acid, $C_6H_4 \diagup{}^{COOH}_{\diagdown COOH}$, occurs in the form of rhombic crystals. By heating phthalic acid, phthalic anhydride may be obtained.

Phthalic anhydride, $C_6H_4 \diagup{}^{CO}_{\diagdown CO}\diagdown O$, heated with phenol and sulphuric acid will give phenolphthalein, a valuable and familiar indicator in volumetric analysis.

Sulphanilic Acid, $C_6H_4 \diagup{}^{HSO_3}_{\diagdown NH_2}$, is made by treating aniline with concentrated sulphuric acid. It is a strong acid, occurring as white crystals, is soluble in water, and is used in the manufacture of aniline dyes and also with naphthylamine as a reagent for the detection of nitrites.

Phenyl Sulphuric Acid, $C_6H_5HSO_4$, occurs only in combination, the acid being unstable if attempt is made to isolate it. Its potassium salt is present in the urine as a product of intestinal putrefaction.

Phenyl-sulphonic Acid may be made by action of oxygen upon the sulph-hydrate, similar to the process described on page 232.

$$C_6H_5SH + 3\,O = C_6H_5SO_2HO.$$
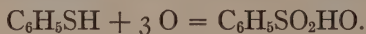
The potassium salt of this acid heated with potassium hydroxide is a commercial source of phenol.

$$C_6H_5.SO_3K + KOH = C_6H_5.OH + K_2SO_3.$$
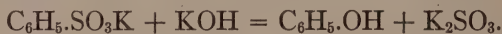
Phenol-sulphonic Acid. — When phenol is treated with several times its volume of cold, strong sulphuric acid, phenol

sulphonic acid, OH⬡ HSO₃ or OH⬡ (with HSO₃ below), results. If the mixture is

heated for some time over a water-bath, the disulphonic acid results. This acid, warmed with a nitrate and the mixture treated with excess of ammonia, yields ammonium picrate, and constitutes a delicate test for nitrates present in drinking water.

Phenol-sulphonic acid has been used in dentistry as a therapeutic agent (as antiseptic and otherwise). Such use is discussed in detail by Herman Prinz, M.D., D.D.S., in the *Dental Cosmos* for April, 1912, with the conclusion that the ortho compound is several times more active than either the meta or para compounds; that a one per cent solution is about equal in antiseptic strength to a one per cent phenol solution, but in this strength it decalcifies the tooth structure, discolors the teeth, and should not be used in the mouth on account of its pronounced acid character.

$$
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{HC} \quad\quad \text{C}\!-\!\!-\!\!-\text{CH} \\
\mid \quad\quad \parallel \quad\quad \parallel \\
\text{HC} \quad\quad \text{C} \quad\quad \text{CH} \\
\text{C} \quad \text{N} \\
\text{H} \quad\quad \text{H}
\end{array}
$$
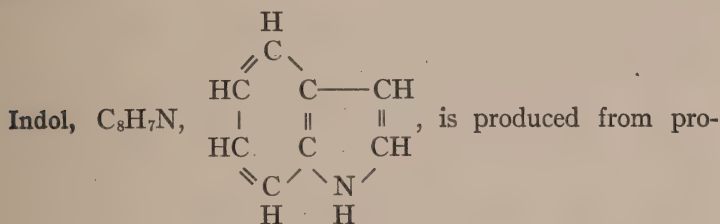
Indol, C_8H_7N, [structural formula], is produced from protein by the putrefaction occurring in the small intestine, also by action of the proteolytic enzyme of the pancreatic juice (trypsin). The indol, by oxidation (after absorption from the intestines), becomes indoxyl, C_8H_6NO, which, with potassium sulphate, forms indoxyl-potassium sulphate, $C_8H_6NKSO_4$, and, as such, is eliminated (in part) by the kidneys. This substance is a type of the so-called ethereal or conjugate sulphates, skatoxyl-potassium sulphate (skatol) and phenol-potassium sulphate being other compounds of this class. The ethereal sulphates are not precipitated by barium chloride in alkaline solutions, but may be decomposed by prolonged boiling with hydrochloric acid and then precipitated as usual.

The oxidation of indoxyl produces indigo blue, and this fact is utilized in the qualitative test for indoxyl in urine (q. v.).

Skatol, methylindol, $C_6H_4 \underset{NH}{\overset{C.CH_3}{<}} > CH$, occurs in similar manner to indoxyl, and likewise passes into the urine as an ethereal sulphate (skatoxyl-potassium sulphate). Skatol is a constituent of the feces and possesses a strong fecal odor.

Heterocyclic Compounds. — The closed-chain or cyclic compounds are known as isocyclic or homocyclic when the atoms constituting the "ring" or nucleus of the molecule are all of the same sort (carbocyclic, if all of carbon), as has been the case in all the aromatic compounds which we have thus far taken up, i.e., the structure of compounds has been based upon the six-carbon or benzene ring. If the ring is made up of atoms of different sorts the compound is heterocyclic, and one or two of these are of importance.

First, pyridin, C_5H_5N, which may be regarded as benzene, in which one CH group has been replaced by an atom of nitrogen:

$$
\begin{array}{c}
H \\
\overset{C}{/} \overset{}{\diagdown} \\
HC \quad\quad CH \\
| \quad\quad\; \| \\
HC \quad\quad CH \\
\diagdown N \diagup
\end{array}
$$
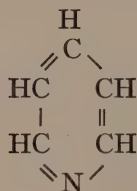
It is a liquid miscible with water, boiling-point 115° C.

Second, quinalin, C_9H_7N, a colorless liquid.

$$
\begin{array}{c}
H \quad\quad H \\
\overset{C}{/}\diagdown \overset{C}{/}\diagdown \\
HC \quad\; C \quad\; CH \\
| \quad\quad | \quad\quad \| \\
HC \quad\; C \quad\; CH \\
\diagdown C \diagup \diagdown N \diagup \\
H
\end{array}
$$
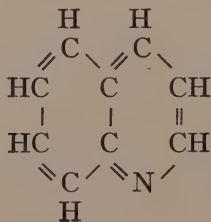
Upon one or the other of these two bases may be constructed the graphic formula of many of the vegetable alkaloids.

A certain number of alkaloids, such as caffein and thein (trimethylxanthin), are referable to the purin nucleus (page 240).

PART VI.

PHYSIOLOGICAL CHEMISTRY.

CHAPTER XXIX.

FERMENTS OR ENZYMES.

PHYSIOLOGICAL chemistry treats of the substances which go to make up the animal body, the changes which these substances undergo in the process of digestion assimilation, and the final products of metabolism.

This subject, like others, will receive our attention in outline, with a view simply to enable the student to understand the conditions which at present seem to have the most direct bearing on dental science. The changes produced by the class of bodies known as ferments are of great importance and the first to be considered.

If yeast is allowed to grow in a sugar solution of moderate strength, the sugar molecule is split into carbonic-acid gas and alcohol. The process is one of fermentation; the yeast is the ferment. There are various substances which cause similar splitting of complex molecules into simpler compounds.*

The distinction between the organized and the unorganized ferments is no longer recognized, as it has been proved that the activity of an organized ferment is due to the presence of the unorganized ferment or enzyme, and we shall, by preference, refer to these substances as enzymes.

The enzymes, as a class, possess certain general properties which should be remembered.

* Occasionally fermentation may produce a synthesis (putting together) rather than an analysis (pulling apart).

First. Their action is limited to a very few substances; i.e., the enzyme from yeast, referred to above, will convert a few sugars only as indicated. They will not act in any other way nor upon other substances.

Second. The enzymes act only at ordinary temperatures, usually showing the greatest activity at about the temperature of the animal body, 37° to 40° C.

Third. Enzymes act only within very narrow limits as regards the chemical reaction (acid or alkaline) of the media.

Fourth. Enzymes are destroyed (killed) by the heat of boiling water.

Fifth. In regard to the nature of their composition, many of the enzymes are closely allied to the proteins.

An enzyme may be classified according to the sort of work it does. Many of the chemical changes involved in the utilization of food consist of breaking up a complex molecule and by the use of a molecule of water forming new and simpler compounds. This sort of change is called "Hydrolysis" and an enzyme which will produce it is a hydrolytic enzyme. By hydrolysis or hydrolytic cleavage, the molecule of cane-sugar, $C_{12}H_{22}O_{11}$, becomes two molecules of a simpler sugar, such as glucose, $C_6H_{12}O_6$. $C_{12}H_{22}O_{11} + H_2O = 2\ C_6H_{12}O_6$.

Hydrolysis is not dependent upon enzyme action, as the same change is produced by prolonged boiling with very dilute mineral acids.

Besides the classification of enzymes by the character of the work they do, the name of the substance acted upon may also be used to designate an enzyme; thus, a proteolytic enzyme produces a cleavage of protein substances. A lipolytic enzyme (lipase) splits the fat molecule, etc.

Several of the digestive enzymes, notably the proteolytic or flesh-digesting enzymes, such as pepsin, trypsin, etc., exist in the animal cell, not as active agents, but as inactive parent enzymes which are called pro-enzymes or zymogens. Enzymes

of this class are set to work (liberated from the parent substance) by a class of substances known as "activators" (illustrated by the enterokinase of the intestine, page 324).

Neither the zymogen nor the activator has of itself any digestive action whatever; a provision which results in the prevention of autodigestion (autolysis) of the cells containing them.

Another large and very important class of enzymes are those which produce oxidative changes. They may be divided into the oxidases, which produce direct oxidation, and the peroxidases, which produce oxidation only in the presence or by the aid of peroxide.

Catalase is a term which has been applied to enzymes, similar in action to the peroxidases; i.e., they destroy a peroxide with the formation of molecular oxygen, although, according to Hammarsten, they differ from both the oxidases and peroxidases in giving no reaction whatever with guaiac.

Oxidases have been found to exist in saliva, in milk, blood, nasal mucus, tears, and semen, in many of the organs, and also in the muscular tissue. They exist moreover in the vegetable kingdom from which the subject of oxidizing enzymes was first studied by Bertrand and Bourquelot.* The urine, bile, and intestinal secretions are said not to contain a ferment of this kind.

The name of a specific enzyme usually ends in "-ase" as zymase, the enzyme contained in yeast; lipase, a fat-splitting enzyme; urease, the urine ferment.

* "Enzymes and their Applications," Effrant: Prescott's translation. This work is also authority for statement immediately preceding regarding the source of oxidizing enzymes.

CHAPTER XXX.

CARBOHYDRATES.

Classification:

Arabinose
Xylose } Pentoses.

Sugars {
Dextrose
Levulose
Galactose } Monosaccharides or monoses.

Saccharose
Maltose
Lactose } Disaccharides or dioses.

Starch {
Starch
Glycogen }

Gum
Cellulose } Dextrin } Polysaccharides or polyoses.

Characteristics. — The monosaccharides are reducing bodies of either the aldehyde or the ketone type. The termination "ose" is applied to all sugars, and may also be used in designating the type; thus dextrose is an "aldose," while levulose is a "ketose;" i.e., dextrose is an aldehyde, containing the characteristic $-CHO$ group, while levulose is a ketone containing the $-C = O$ group.

The pentoses ($C_5H_{10}O_5$) are represented by two important compounds, arabinose and xylose. The first of these occurs occasionally in the urine (pentosuria), and can be prepared by boiling gum arabic with dilute mineral acids. The second, xylose, has been obtained from the pancreas, but may be pre-

259

pared more easily from bran or straw by boiling with dilute hydrochloric acid (Exp. 162, page 400).

The pentoses, as a class, boiled with dilute mineral acid (hydrochloric or sulphuric), yield furfuraldehyde by splitting off the elements of three molecules of water:

$$C_5H_{10}O_5 - 3\ H_2O = C_5H_4O_2.$$

The formation of furfuraldehyde can be easily demonstrated by various color reactions as given in experiment 162, page 400.

The hexoses, $C_6H_{12}O_6$, also called monoses, occur quite generally in nature (not true of the pentoses). They constitute the various fruit sugars, and may be obtained by hydrolysis of the dioses and polyoses.

They all reduce Fehling's copper solution (galactose less easily than the others), and they are all fermented by yeast (galactose more slowly than the others).

Dextrose or **Glucose**, $C_6H_{12}O_6$, also known as grape-sugar and as diabetic sugar, occurs in grapes, honey, etc. It is formed by the action of diastatic ferments on the disaccharides; also from many of the polysaccharides. Glucose thus occurs in the processes of digestion and constitutes the sugar of diabetic urine. It may be obtained commercially as a white solid, and also as a thick, heavy syrup, known as confectioners' glucose. The commercial glucose is prepared by the action of dilute acids on starch, when hydrolysis takes place, as follows:

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6.$$

Dextrose can be oxidized first to gluconic acid ($CH_2OH.-(CHOH)_4.COOH$), and by further oxidation to diabasic saccharic acid:

$$COOH.(CHOH)_4.COOH.$$

This oxidation can be effected by the use of nitric acid. Saccharic acid forms a definite soluble salt with calcium. Whether

the fact has any bearing whatever on the relation of poor teeth and excessive use of candy has not been demonstrated.

Tests. — Glucose boiled with Fehling's solution precipitates the red suboxide of copper (Cu_2O).

Glucose responds to Molisch's test for carbohydrates, which is made with an alcoholic solution of α-naphthol and concentrated sulphuric acid (Exp. 164). The monosaccharides, of which glucose is a convenient representative, may be distinguished from the other carbohydrates by heating with Barfoed's solution (copper acetate in dilute acetic acid), which is reduced with precipitation of cuprous oxide.

Heated with phenylhydrazine solution nearly to the boiling-point of water, glucose forms phenylglucosazone, which crystallizes, as the mixture cools, in characteristic yellow needles usually arranged in bundles or sheaves. (Plate VI, Fig. 1.)

Osazones are the various compounds formed by the different sugars and phenylhydrazine when treated as above. They crystallize in fairly distinctive forms and furnish valuable tests for the sugars. The phenylhydrazine test is considered at least ten times more delicate than Fehling's test. Glucose readily undergoes alcoholic fermentation, yielding C_2H_5OH and CO_2. (See Exp. 172, page 401.)

Levulose, $C_6H_{12}O_6$, or fruit-sugar, turns the ray of polarized light to the left, and to a greater degree than glucose turns it to the right. It occurs in honey and in many fruits, and is produced with glucose by hydrolysis of cane-sugar. Levulose forms an osazone not to be distinguished from glucosazone. It reduces copper solutions in a manner similar to glucose, and, like it, is easily fermented by yeast.

Galactose is the product of the hydrolysis of lactose, or milk-sugar, and some other carbohydrates. It is a crystalline substance which reduces Fehling's solution and ferments slowly with yeast.

DISACCHARIDES OR DIOSES.

Disaccharides have the general formula $C_{12}H_{22}O_{11}$. They are converted into the monosaccharides by hydrolysis brought about either by action of enzymes or by boiling with mineral acid.

Cane-sugar, $C_{12}H_{22}O_{11}$, sucrose or saccharose, obtained from the sugar-cane (various varieties of sorghum), also from the sugar-beet (*Beta vulgaris*) and the sugar-maple (*Acer saccharinum*). Cane-sugar is a white crystalline solid soluble in about 1/2 part of water and in 175 parts of alcohol (U. S. P.). It does not reduce copper solutions, nor does it form an osazone with phenylhydrazine; but it is easily hydrolyzed with the formation of dextrose and levulose, and then, of course, the reactions peculiar to these substances may be obtained. It does not ferment directly, but, by the action of invertin contained in yeast, it takes up water, becoming glucose and levulose as above, these latter sugars being easily fermentable.

Maltose, $C_{12}H_{22}O_{11}$, or malt-sugar, is an intermediate product in the hydrolysis of starch, and by further hydration becomes two molecules of dextrose: $C_{12}H_{22}O_{11} + H_2O = 2\ C_6H_{12}O_6$. It is formed in the fermentation of barley by diastase (the ferment of malt), and with phenylhydrazine it produces an osazone distinguished from glucosazone and lactosazone by its microscopical appearance (Plate VI, Fig. 2) and its melting-point.

Lactose, $C_{12}H_{22}O_{11}$, obtained from milk, is a disaccharide with far less sweetening power than sucrose. It forms an osazone which crystallizes in small burr-shaped forms (Plate VI, Fig. 3). It reduces Fehling's solution, but does not reduce Barfoed's solution. It resists fermentation in a marked degree. Upon hydration it is converted into dextrose and galactose.

POLYOSES — POLYSACCHARIDES.

Starch. — This well-known and widely distributed plant-constituent is a carbohydrate represented by $C_6H_{10}O_5$, the actual molecule, however, being many times this simple formula. The

PLATE VI. — PHYSIOLOGICAL CHEMISTRY
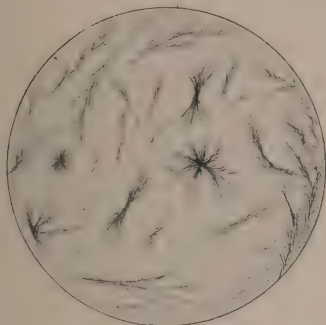
FIG. 1.
Glucosazone.
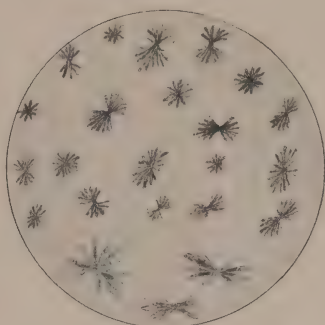
FIG. 2.
Maltosazone.
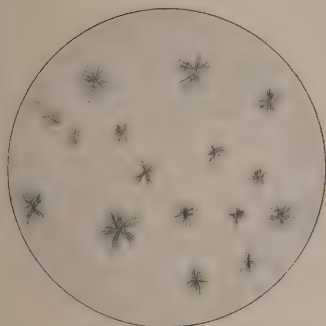
FIG. 3.
Lactosazone.
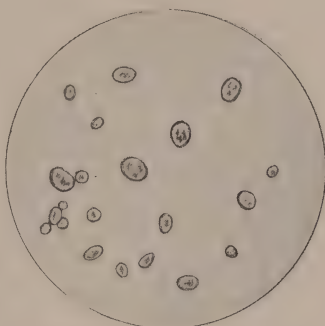
FIG. 4.
Wheat Starch.
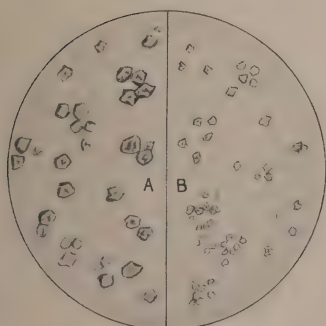
FIG. 5.
A, Corn starch; *B*, Rice starch.

FIG. 6.
A, Potato starch; *B*, Arrowroot starch.

microscopical appearance of the starch granule is quite characteristic, and recognition of the more common starches by this method is not at all difficult (see Plate VI, page 262).

Starch is not soluble in cold water, but in hot water, or in solutions containing "amylolytic" enzymes, or in solutions containing certain chemical substances, as chloride of zinc or of magnesium, dilute hydrochloric or sulphuric acid, capable of forming hydrolytic products, the starch granules swell up, and ultimately dissolve, being converted into dextrose. The conversion, however, takes place in several well-defined steps, as follows: Soluble starch is first formed, answering the same chemical test with iodine (Exp. 245, page 416); next, *erythrodextrin*, which gives a red color with iodine solution; then *achroo-* and *maltodextrin*, which give no color with iodine, but react slightly with Fehling's copper solution; then *maltose*, also negative with iodine, but reacting strongly with Fehling's solution; and finally *dextrose*.

Dextrin ($C_6H_{10}O_5$) is a yellowish powder, also known as British gum; is formed from starch, as indicated above; constitutes to a considerable extent the "crust" of bread; is soluble in water, the solution giving a red color with iodine, and is also distinguished from starch by its failure to give a precipitate with solution of tannic acid.

Glycogen, or animal starch, is a carbohydrate, with the general formula $C_6H_{10}O_5$, occurring *principally* in the liver, and to a lesser extent in nearly all parts of the animal body. Freshly opened oysters are a convenient source of the substance for laboratory demonstration. It occurs in horse-flesh in considerably larger proportions than in human flesh.

Properties. — Glycogen is a white powder without odor or taste. It dissolves in water, producing an opalescent solution. It is closely allied to the starches of vegetable origin in that the products of its hydrolysis are dextrin * and ultimately dextrose.

* Foster's Text-book of Physiology.

It differs in its ready solubility in water, and in the fact that it is precipitated by 66% alcohol, also in its power of rotation, which is much stronger than that of starch.

Physiology. — Glycogen is formed by the liver, and stored by this same organ for future use. It is derived principally from carbohydrates, but may also be derived from proteins. It disappears during starvation. In dead liver or muscle it rapidly undergoes hydrolytic change with the production of a reducing sugar.

Cellulose, $C_6H_{10}O_5$, is a carbohydrate which occurs as a principal constituent of woody fiber, and which may be found in the laboratory in nearly a pure state, as absorbent cotton or Swedish filter-paper. It is insoluble in water, alcohol, or dilute acids; it may be dissolved, however, by an ammoniacal copper solution. It is converted into monosaccharides by acids, only after first treating with concentrated sulphuric acid, which partially dissolves it. Cellulose aids digestion in a purely mechanical way by separating the digestible matter and allowing easier access of digestive ferments. The celluloses may be divided into three classes: those resisting hydrolysis and consequently lacking nutritive value, such as flax, cotton fibers, and hemp; those which hydrolyze slightly, which include the ligno-celluloses and may be utilized as food by herbiverous animals; the pseudo-celluloses, which are hydrolysed quite easily and may be digested by enzymes.

When cellulose is treated with a mixture of nitric and sulphuric acids, it is converted into nitro-substitution products which are known as guncotton. The soluble cotton from which collodion is prepared, by solution in a mixture of ether and alcohol, is a mixture of tetra- and pentanitrates, while the more explosive but insoluble guncotton is a hexanitrate, formerly known as trinitrocellulose.

CHAPTER XXXI.

FATS AND OILS.

NATURAL fats and oils of animal or vegetable origin are mixtures of several compound glyceryl ethers or esters (see page 215), and by subjecting them to cold and pressure they may be separated into two portions, one solid with comparatively high melting-point, and the other liquid at ordinary temperatures. The solid portion is known as the stearopten, and the liquid as the eleopten, of the fat. Thus from beef-fat, we may express a fluid eleopten consisting largely of olein and obtain as a residue a stearopten, stearin. The stearopten of the volatile or essential oils are classed as camphors, on account of their resemblance to ordinary camphor. Menthol, from oil of peppermint, and thymol, from oil of thyme, are examples of this class of compounds, both of which are largely used in dental practice.

Properties. — Fats are insoluble in water, easily dissolved by ether, chloroform, and carbon disulphide, less easily by alcohol, crystallizing on evaporation of the solvent. (Plate VII, Fig. 3, page 287.) They are emulsified by mechanical subdivision of the fat globules, in the presence of some agent which prevents their reuniting. The vegetable mucilages, soap, jelly, etc., are such emulsifying agents. On exposure to the air, fats and oils are more or less easily oxidized, which causes a separation of the fat acid. This produces an unpleasant odor or taste, and the fat is said to become rancid.

Chemistry. — The principal organic acids entering into the composition of fat are Stearic acid, $HC_{18}H_{35}O_2$, solid, white, without odor or taste, melts at 70° C.; Palmitic acid, $HC_{16}H_{31}O_2$,

resembles stearic acid in its physical properties but melts at 62° C.; Oleic acid, $HC_{18}H_3O_2$, contains two $CH=$ groups with double-bonded carbons in the middle of the chain. This last acid is fluid at ordinary temperatures and predominates in the softer animal fat. Its glyceryl ester, olein, constitutes seventy to eighty-five per cent. of human fat (percentage said to increase with age) and thirty-six per cent. of butter.

Physiology. — Fats are not digested to any appreciable extent until they reach the intestine; here they are broken up by a fat-splitting enzyme, emulsified, and to a slight extent saponified, after which they may be absorbed by the system (see Pancreatic Digest on).

Glyceryl Palmitate, $C_3H_5(C_{16}H_{31}O_2)_3$, tripalmitin; **glyceryl stearate,** $C_3H_5(C_{18}H_{35}O_2)_3$, tristearin, and **glyceryl oleate,** $C_3H_5(C_{18}H_{33}O_2)_3$, triolein; these in varying proportions make up the greater part of animal and vegetable fats and oils.

The prefix "tri" is used because the "mono" and "di" compounds, as monopalmitin, $C_3H_5(OH)_2 - C_{16}H_{31}O_2$, etc., are possible and may be prepared by synthesis. Triolein is liquid at ordinary temperature, solidifies at $-6°$ C., is a "double-bonded" compound, hence forms addition-products with the halogens as stearin and palmitin cannot do, since they are "saturated hydrocarbons."

The amount of chlorine or bromine which a fat or oil can thus absorb is an index of the proportion of unsaturated fatty acids contained in it, and hence becomes a valuable method of identification. Olive-oil and lard-oil contain large amounts of olein.

Tripalmitin melts at 66° C., is usually obtained from palm-oil. Tristearin melts at 72° C., occurs with palmitin and olein in beef-fat, mutton-tallow, etc., the consistence of the fat being dependent upon the proportions of the constituent esters.

The fats, stearin for example, may be split into glycerol and fatty acid by steam under pressure as follows:

$$C_3H_5(C_{18}H_{35}O_2)_3 + 3\ H_2O = C_3H_5(OH)_3 + 3\ HC_{18}H_{35}O_2.$$
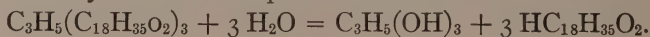
A partial result of this sort is brought about by the fat-splitting enzyme (lipase) of the pancreatic juice (see Steapsin).

Saponification of the fats by caustic alkali takes place as follows:

$$C_3H_5(C_{18}H_{35}O_2)_3 + 3\ KOH = C_3H_5(OH)_3 + 3\ KC_{18}H_{35}O_2.$$

The potassium salts of the fatty acids constitute the soft soaps, while the sodium salts are in general the hard soaps. The "salting-out" process in soap manufacture brings about a double decomposition resulting in the production of ordinary soap.

Volatile Oils do not contain the glyceryl base but rather a group of hydrocarbons known as the " terpenes." The formula is $(C_5H_8)_2$, the most important of the group is $C_{10}H_{16}$ from oil of turpentine and many of the essential oils.

The odor of the volatile oils seems to be dependent upon the presence of water and air; for example, oil of clove distilled over lime and in atmosphere free from oxygen has little odor. The presence of oxygen and moisture restores the characteristic odor.

Lecithin has been classified as a phosphorized fat; it occurs in nervous tissue, in the bile, and is obtained in considerable quantity from the yolk of eggs. It contains two fat acid radicals combined with glycerol, phosphoric acid and choline. Lecithin is soluble in chloroform, alcohol, ether and benzene, and may be obtained in crystalline form from the alcoholic solution. The fatty acid radicals are not always the same or necessarily alike. Lecithin may be represented by the following formula:

$$
\begin{array}{l}
CH_2 - C_{17}H_{35}CO_2 \\
\quad | \\
CH\ -C_{17}H_{33}CO_2 \\
\quad | \\
CH_2O \\
\qquad | \\
O = P\ -OH.O \\
\qquad\quad | \\
\qquad\quad C_2H_4 \\
\qquad\quad | \\
\quad (CH_3)_3N-OH
\end{array}
$$
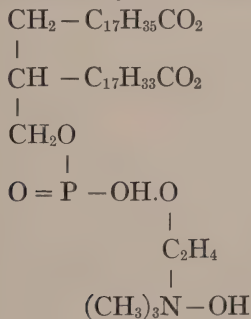
and its decomposition by the following reaction:

$$C_{44}H_{90}NPO_9 + 3\ H_2O = 2\ C_{18}H_{36}O_2 + C_3H_9PO_6 + C_5H_{15}NO_2$$
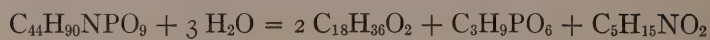
| Lecithin | Stearic acid | Glycero-phosphoric acid | Choline |

CHAPTER XXXII.

PROTEINS.

PROTEIN * is a general term used to designate the nitrogenized bodies which constitute the greater proportion of animal tissue.

While meat and "protein" are usually associated, it must not be forgotten that meat is not the exclusive source of protein, for we usually find protein in vegetable substances and often to a considerable extent.

Unlike the other two great divisions of food substances (carbohydrates and fats), the structure of the protein molecule is so complex that with a few exceptions of the simplest kind its representation has not been attempted.

The protein molecule contains nitrogen (often as the amino group NH_2) in addition to the carbon, hydrogen, and oxygen of the carbohydrates and fats. It frequently contains sulphur, often phosphorus, and occasionally the metallic elements, particularly iron.

As examples of the complexity of protein molecules, the following proposed formulæ are given in Hawk's Physiological Chemistry.

Serum albumin, $C_{450}H_{720}N_{116}S_6O_{140}$.

Oxyhemoglobin, $C_{658}H_{1181}N_{207}S_2FeO_{210}$.

While a classification of proteins according to their chemical composition is at present practically impossible, the following may be of interest.

After Hofmeister, Ergebnisse der Physiologie, Jahrg. I.

* The term proteid was formerly used instead of protein, but in accordance with the recommendations of the Committees of the American Physiological and Biochemical Societies, it has been abandoned. The classification and definitions herewith given are taken from their recommendation as printed in Science, Vol. 27, No. 692, page 554.

I. Groups of the Aliphatic Series.

A. Group containing C, N, H.

The only representative known is the guanidine radical $(CNH).NH_2$.

B. Groups containing C, N, H, O.

1. Amino-acids.

(a) Monamino-acids.

1. Monobasic monamino-acids, $C_nH_{2n+1}NO_2$.

C_2 is glycocoll.

C_3 is alanin.

C_5 is aminovalerianic acid.

C_6 is leucine, which occurs universally.

2. Dibasic monamino-acids, $C_nH_{2n-1}NO_4$.

C_4 is asparaginic acid.

C_5 is glutaminic acid.

(b) Diamino-acids (all monobasic acids).

C_2 is diaminoacetic acid (rare).

Argynine (guanidine-α-aminovalerianic acid). Here the diamino-acid is combined with the guanidine radical,

$$NH_2.NH.C.NH.CH_2.(CH_2)_2.CH.NH_2COOH.$$
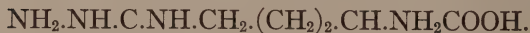
Lysine (α-ϵ-diaminocapronic acid),

$$NH_2.CH_2.(CH_2)_3.CH.NH_2.COOH.$$
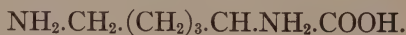
2. Amino-alcohols.

Glucosamine, $C_6H_{11}O_5(NH_2)$, a hexose into which NH_2 has entered the carbohydrate group of the protein molecule.

C. Groups containing C, N, H, O, S.

Cystein, aminothiolactic acid, $CH_2.SH.CH(NH_2).COOH$.

Cystin, the sulphide of cystein, $C_6H_{12}S_2N_2O_4$.

α-thiolactic acid.

II. Groups of the Aromatic Series.

A. Phenylalanin, $C_6H_5.CH_2.CH(NH_2).COOH$.

B. Tyrosin, $C_6H_4.OH.CH_2.CH(NH_2).COOH$.

III.

A. Pyrrol group.

    1. α-pyrrolidine carbonic acid,

$$CH-CH-CH-CH.COOH$$
$$\vert \underline{\hspace{2em}-NH\hspace{2em}} \vert$$
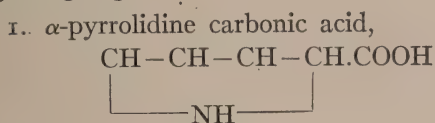
B. Indol group.

    1. Indol, see page 253.

    2. Skatol (methyl indol), see page 254.

    3. Tryptophane (indolaminopropionic acid), $C_{11}H_{12}N_2O_2$.

    4. Skatosin, $C_{10}H_{16}N_2O_2$.

C. Pyridin group.

    Pyridin, see structural formula on page 254.

D. Pyrimidin group.

    Histidin: structural formula probably

$$NH\underline{\hspace{2em}}CH$$
$$\vert \qquad\quad \Vert$$
$$CH = C-N-CH_2-CHNH_2-COOH.$$
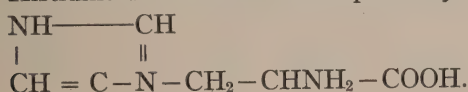
Excepting the carbohydrate group, and perhaps the pyridin and pyrimidin groups, which are absent in a few special instances, all typical proteins contain at least one representative from each group.

A much more practical classification, based in part upon the *properties* of the substance, is that suggested by the Joint Committees on Protein Nomenclature (footnote, page 269).

"Since a chemical basis for the nomenclature of the proteins

is at present not possible, it seems important to recommend a few changes in the names and definitions of generally accepted groups, even though, in many cases, these are not wholly satisfactory." The recommendations are as follows:

First. The word proteid should be abandoned.

Second. The word protein should designate that group of substances which consist, so far as is known at present, essentially of combinations of α-amino acids and their derivatives, e.g., α-aminoacetic acid or glycocoll; α-amino propionic acid or alanin; phenyl-α-amino propionic acid or phenylalanin; guanidine-amino valerianic acid or arginine, etc., and are therefore essentially polypeptides.

Third. That the following terms be used to designate the various groups of proteins:

I. Simple Proteins.

Protein substances which yield only α-amino acids or their derivatives on hydrolysis.

Although no means are at present available whereby the chemical individuality of any protein can be established, a number of simple proteins have been isolated from animal and vegetable tissues which have been so well characterized by constancy of ultimate composition and uniformity of physical properties that they may be treated as chemical individuals until further knowledge makes it possible to characterize them more definitely.

The various groups of simple proteins may be designated as follows:

(a) *Albumins.* — Simple proteins soluble in pure water and coagulable by heat; e.g., ovalbumin, serum albumin, lactalbumin, vegetable albumins.

(b) *Globulins.* — Simple proteins insoluble in pure water, but soluble in neutral solutions of salts of strong bases with strong

acids;* e.g.,† serum globulin, ovoglobulin, edestin, amandin, and other vegetable globulins.

(*c*) *Glutelins.* — Simple proteins insoluble in all neutral solvents but readily soluble in very dilute acids and alkalies;‡ e.g., glutenin.

(*d*) *Alcohol-soluble Proteins* (*Prolamines*). — Simple proteins soluble in relatively strong alcohol (70 to 80 per cent), but insoluble in water, absolute alcohol, and other neutral solvents;§ e.g., zein, gliadin, hordein, and bynin.

(*e*) *Albuminoids.* — Simple proteins which possess essentially the same chemical structure as the other proteins, but are characterized by great insolubility in all neutral solvents;‖ e.g., elastin, collagen, keratin.

(*f*) *Histones.* — Soluble in water and insoluble in very dilute ammonia and, in the absence of ammonium salts, insoluble even in an excess of ammonia; yield precipitates with solutions of other proteins and a coagulum on heating which is easily soluble · in very dilute acids. On hydrolysis they yield a large number of amino acids, among which the basic ones predominate; e.g., globin, thymus histone, scombrone.

(*g*) *Protamines.* — Simpler polypeptides than the proteins included in the preceding groups. They are soluble in water, uncoagulable by heat, have the property of precipitating aqueous solutions of other proteins, possess strong basic properties and

* The precipitation limits with ammonium sulphate should not be made a basis for distinguishing the albumins from the globulins.

† The examples of the various proteins are those given by Prof. P. B. Hawk.

‡ Such substances occur in abundance in the seeds of cereals and doubtless represent a well-defined natural group of simple proteins.

§ The sub-classes defined (*a, b, c, d*) are exemplified by proteins obtained from both plants and animals. The use of appropriate prefixes will suffice to indicate the origin of the compounds, e.g., ovoglobulin, myoalbumin, etc.

‖ These form the principal organic constituents of the skeletal structure of animals and also their external covering and its appendages. This definition does not provide for gelatin, which is, however, an artificial derivative of collagen.

form stable salts with strong mineral acids. They yield comparatively few amino acids, among which the basic amino acids greatly predominate; e.g., salmine, sturine, clupeine, scombrine.

II. Conjugated Proteins.

Substances which contain the protein molecule united to some other molecule or molecules otherwise than as a salt.

(*a*) *Nucleoproteins.* — Compounds of one or more protein molecules with nucleic acid; e.g., cystoglobulin, nucleohistone.

(*b*) *Glycoproteins.* — Compounds of the protein molecule with a substance or substances containing a carbohydrate group other than a nucleic acid; e.g., mucins and mucoids (osseomucoid, tendomucoid, ichthulin, helicoprotein).

(*c*) *Phosphoproteins.* — Compounds of the protein molecule with some, as yet undefined, phosphorus-containing substance other than a nucleic acid or lecithins;* e.g., caseinogen, vitellin.

(*d*) *Hemoglobins.* — Compounds of the protein molecule with hematin or some similar substance; e.g., hemoglobin, hemocyanin.

(*e*) *Lecithoproteins.* — Compounds of the protein molecule with lecithins (lecithans, phosphatides); e.g., lecithans, phosphatides.

III. Derived Proteins.

1. *Primary Protein Derivatives.* — Derivatives of the protein molecule apparently formed through hydrolytic changes which involve only slight alterations of the protein molecule.

(*a*) *Proteans.* — Insoluble products which apparently result from the incipient action of water, very dilute acids or enzymes; e.g., myosan, edestan.

(*b*) *Metaproteins.* — Products of the further action of acids

* The accumulated chemical evidence distinctly points to the propriety of classifying the phosphoproteins as conjugated compounds; i.e., they are possibly esters of some phosphoric acid or acids and protein.

and alkalies whereby the molecule is so far altered as to form products soluble in very weak acids and alkalies, but insoluble in neutral fluids.

This group will thus include the familiar "acid proteins" and "alkali proteins," not the salts of proteins with acids; e.g., acid metaproteins (acid albuminate), alkali metaprotein (alkali albuminate).

(c) *Coagulated Proteins.* — Insoluble products which result from (1) the action of heat on their solutions, or (2) the action of alcohols on the protein.

2. *Secondary Protein Derivatives.** — Products of the further hydrolytic cleavage of the protein molecule.

(a) *Proteoses.* — Soluble in water, uncoagulated by heat, and precipitated by saturating their solutions with ammonium sulphate or zinc sulphate;† e.g., protoproteose, deuteroproteose.

(b) *Peptones.* — Soluble in water, uncoagulated by heat, but not precipitated by saturating their solutions with ammonium sulphate;‡ e.g., antipeptone, amphopeptone.

(c) *Peptides.* — Definitely characterized combinations of two or more amino acids, the carboxyl group of one being united with the amino group of the other, with the elimination of a molecule of water; § e.g., dipeptides, tripeptides, tetrapeptides, pentapeptides.

Albumins.

The albumins are conveniently represented by egg-albumin and serum-albumin. They are soluble in water, respond to the

* The term *secondary hydrolytic derivatives* is used because the formation of the primary derivatives usually precedes the formation of these secondary derivatives.

† As thus defined, this term does not strictly cover all the protein derivatives commonly called proteoses; e.g., heteroproteose and dysproteose.

‡ In this group the kyrins may be included. For the present we believe that it will be helpful to retain this term as defined, reserving the expression peptide for the simpler compounds of definite structure, such as dipeptides, etc.

§ The peptones are undoubtedly peptides or mixtures of peptides, the latter being at present used to designate those of definite structure.

general protein reactions (Exp. 187, page 405, etc.), and may be completely precipitated by saturation of the solution by ammonium sulphate. Albumin is coagulated by heat (75° to 80° C.).

Egg-albumin differs from serum-albumin in that it is not absorbed when injected into the circulation, but appears unchanged in the urine. Egg-albumin is readily precipitated from aqueous solution by alcohol, while serum-albumin is precipitated only with difficulty. Albumins in general form, with acids or with alkalies, *derived albumins* known as acid or alkali albumins or albuminates (acid or alkali metaproteins). An acid albumin derived from myosin is known as syntonin. It differs but slightly from other acid albumins. The acid and alkali albumins are both precipitated by neutralization, but neither of them are coagulated by heat.

If the hydrolysis of albumin is brought about by hydrochloric acid at the body temperature, it causes the molecule to split into two proteins, one known as antialbuminate and the other as hemialbumose, these in turn becoming respectively antialbumid and hemipeptone. Sulphuric acid at a boiling temperature produces a similar change, except that the hemipeptone is further changed to leucin and tyrosin. Digestive ferments, pepsin, and trypsin produce antialbumose, hemiantipeptone, and hemialbumose, but trypsin alone converts the hemipeptone into leucin and tyrosin.

Albumin normally occurs in all the body fluids except in the urine. The amount in milk is extremely slight; the amount in saliva seems to vary in inverse proportion to mucin. Albumin occurring in urine in appreciable quantity is always abnormal, although in many cases it has no serious significance unless persistently present in more than the slightest possible trace.

GLOBULINS.

The globulins occur in both plants and animals, and crushed hemp seed may be used as a convenient source for laboratory experiment. It is also associated with albumin in blood-plasma,

and may be separated from it by half saturation with ammonium sulphate, which precipitates the globulin only, but it is not to be distinguished by the ordinary protein tests and reactions. The albumin of albuminous urine always consists of a mixture of these two proteins, globulin and albumin, not, however, always in the same proportion. The globulins are not soluble in distilled water as the albumins are, but a very small quantity of neutral salt, such as sodium chloride, will serve to effect the solution. Globulin is thrown out of solution by action of carbon dioxide as a white flocculent precipitate. By dialysis the inorganic salts necessary for its solution will be removed and the protein will be precipitated. It is also thrown out by saturation of sodium chloride or magnesium sulphate. Globulin is coagulated by heat at practically the same temperature as serum-albumin; i.e., 75° C.

THE GLUTELINS AND PROLAMINES thus far studied have been mostly obtained from vegetable sources.

Glutenin constitutes about one-half of wheat gluten, and the prolamines mentioned on page 273; Zein is obtained from maize, Hordein from barley, Gliadin from wheat or rye, and Bynin from malt.

ALBUMINOIDS.

Albuminoids are the simple proteins characterized by pronounced insolubility in al neutral salivas, and the common examples are Keratin, from nails and hoofs, etc.; Collagen, from bone and connective tissue; and Elastin, from tendons and ligaments.

The differences in these substances are slight, the keratin being less soluble and less easily acted upon by digestive ferments than either of the other two. Keratin also contains more sulphur. It is the principal constituent of horn, nails, hair, feathers, egg membrane, and some shells, such as turtle and tortoise. The sulphur content of these various sources differs considerably,

ranging from about 5% in hair, about 3% in nail and horn, to 1.4% in egg membrane.

The *keratins* are characterized by the fact that the sulphur which they contain is loosely combined; i.e., easily separated by the formation of hydrogen sulphide and other sulphur compounds as proved by experiment No. 207. The keratins are insoluble in dilute acids and unaffected by any of the digestive ferments; they do, however, dissolve in the caustic alkali solutions, and may be used as the source of leucin, tyrosin, cystin, and other well-known products of protein digestion.

Keratins heated with water, under pressure, to 150° C. will decompose with the formation of mercaptan, hydrogen sulphide, and a substance resembling the proteoses.

Collagen, upon hydrolization with boiling water, produces gelatin, which is a characteristic property of this class of proteins. It may be dissolved by both the gastric and pancreatic juices, especially if previously treated with warm acidulated water. Collagen contains less sulphur than keratin and is obtained particularly from the *tendo Achillis* which contains about 32% of this albuminoid and 63% of water. Collagen responds to the general color tests for the proteins.

Elastin contains the least sulphur of any of the three substances which we have considered. It may be obtained from the ligamentum nuchæ of an ox, which contains about $31\frac{10}{2}\%$ of elastin and 58% of water, by chopping the ligament finely and extracting for two or three days with *half*-saturated solution of calcium hydroxide. Like collagen, it is dissolved upon prolonged treatment with proteolytic ferments.

Reticulin occurs as a fibrous part of lymph glands. It is insoluble in water and is not digested by pepsin or trypsin. It does not respond to Millon's test for proteins.

BONE.

If all organic matter is burned off from bone, there remains the bone-earth, so-called, made up of the phosphates and carbonates of lime and magnesia, with slight amounts of chlorine, fluorine, and of sulphates, the proportion being practically the same as given for dentine, under Teeth, on page 189. Because in some diseases, in which the bones are softened or decalcified (as osteomalacia), the relation of the calcium oxide and phosphorous pentoxide remains unchanged, it has been claimed that these substances exist in the bone in the form of a definite phosphate-carbonate containing three molecules of the tribasic phosphate to one of carbonate: $3 \ Ca_3(PO_4)_2.CaCO_3$.

If, by treatment with dilute hydrochloric acid, the mineral constituents are entirely dissolved out of bone, there remains a substance from which glue (gelatin) is derived, of similar composition to collagen, from connective tissue, and known as *ossein*. Neither of these (ossein or collagen) is soluble in water or in dilute acids.

Bone Marrow is of two sorts, red or yellow. The red marrow contains erythrocytes, fat, lecithin, protein substance consisting of a globulin, a nucleo-protein, fibrinogen, traces of albumin and proteose.

The yellow marrow is similar in composition, except that it contains fewer erythrocytes, more fat and more olein in the fat.

Gelatin is made by hydrolysis of ossein or collagen brought about by *prolonged* boiling with dilute mineral acids. Gelatin, if first treated with cold water till soft, may be dissolved in hot water. The solution is precipitated by mercuric chloride, alcohol, tannic, and picric acids. It responds but feebly to the general protein reactions, but, by digestion with either pepsin or trypsin, compounds are obtained analogous to those resulting from similar protein digestion.

Gelatin solutions respond to the biuret test, not to Millon's nor to the Hopkins-Cole test.

CONJUGATED PROTEINS.

These are substances which contain the protein molecule united to some other molecule or molecules otherwise than as a salt. The conjugated proteins which we shall study are mucin, a type of glyco-protein, yielding upon decomposition a substance containing a carbohydrate group; caseinogen (from milk), a phosphorus-containing substance; and hemoglobin (from blood).

The glyco-protein, mucin, a selected type of this class of protein substance, occurs in various forms in saliva, in urine, bile, and other body fluids. The mucin substances are differentiated from the true mucins, according to Hammarsten, by the fact that the latter form mucilaginous or ropy solutions by the aid of a trace of alkali, from which they are precipitated by acetic acid. The precipitate is insoluble in excess of acid, or soluble only with great difficulty.

True mucins have been separated and examined from the secretion of the submaxillary glands, from snails, from mucous membranes of the air passages, from synovial fluid, and from the navel cord.

Mucin is quite readily converted to metaprotein by boiling with dilute acid, and, by action of strong acid, will yield a number of the simpler amino acids. Mucin itself is acid in reaction, but there is no evidence that it has power to form salts.

The mucins are insoluble in pure water, but dissolve upon the addition of traces of alkali. The solution thus obtained will give the usual color reactions for the proteins.

The action of mucin as a factor in dental caries, formation of gelatinous plaques, etc., will be discussed under Saliva.

Caseinogen, the second conjugated protein which we shall consider, is the principal nitrogenous constituent of milk and will be studied as such.

MILK.

Milk is the characteristic secretion of mammals and contains the three great classes of food material, viz.: the proteins, carbohydrates, and fats. The fat is held as a permanent emulsion in so-called milk plasma.

The plasma consists of water holding in solution caseinogen, albumin with a trace of globulin, milk sugar (lactose), and mineral salts.

Specific Gravity. — Milk contains two different sorts of substances influencing the gravity; first, the fat being lighter than the water tends to decrease the gravity; second, the solids not fat which are heavier than water tend to increase the gravity of the milk. Consequently, it may happen that a very poor milk and a very rich milk will have the same specific gravity; e.g., the normal gravity of whole milk is about 1.031, while the gravity of skim milk will be about 1.035 or 1.036, and that in which cream occurs in large amount may be as low as 1.015 or 1.020. It can be easily seen that starting with whole milk, the addition of cream or the addition of water will both alike reduce the gravity. Hence, taken alone, the gravity tells little or nothing as regards the quality of milk; but, if the gravity is taken together with the fat content, the *two* factors give oftentimes sufficient information.

The relation between the gravity of the fat and the total solids is approximately constant, and the following formula will give the amount of total solids usually within 0.10 or 0.15 of 1%.

$$\text{Total solids} = \frac{\text{Fat} \times 6}{5} + \frac{\text{Sp. gr.}}{4} + 0.46.$$

Reaction. — The reaction of cow's milk, when perfectly fresh, is amphoteric to litmus; i.e., it will both redden blue litmus paper and turn red litmus blue at the same time. This double

reaction is due to the presence of various salts, probably the acid and alkaline phosphates.

Cow's milk is acid to phenolphthalein, and this acidity naturally increases by the multiplication of various acid-forming bacteria, which produce lactic acid by hydrolysis of the milk sugar. When the acid strength has increased sufficiently, the caseinogen is decomposed, and casein is produced and precipitated.

This casein constitutes the curd, and the process is the ordinary souring of milk.

Lactic acid is not the only acid produced in the spontaneous fermentation of milk, as traces of formic, acetic, butyric, and succinic acids have been demonstrated by different investigators.

The degree of acidity of milk is conveniently determined as suggested by W. Thorner (Chem. Zeit., 1891, page 1108, abst. analyst XVI, 200), 10 c.c. of milk with an equal volume of water and a few drops of phenolphthalein as indicator, are titrated with N/10 alkali and every tenth of a degree of alkali used is considered as representing one "degree" of acidity.

By experimenting on samples kept under various conditions, Thorner found that milk coagulates on boiling when the acidity reaches 23°. Adopting 20° as the permissible limit of acidity, he proposes the following test: 10 c.c. of milk, 20 c.c. of water, a few drops of indicator, and 2 c.c. of decinormal alkali are thoroughly mixed; if any red color, however weak, results, the milk will not coagulate upon boiling.*

This method is given partly for its own sake and partly because exactly the same method is used by Dr. Eugene S. Talbot of Chicago and many others for the determination of acidity of urine. By slight modification it may be used for saliva. The record of slight amounts of acidity made in degrees in this way has several practical points in its favor.

* From Allen's Commercial Organic Analysis, Vol. 4.

Casein is the principal protein found in milk. It exists in combination with calcium salts as caseinogen. This combination is broken up and the casein precipitated by the action of rennin and other enzymes, by acids, and by certain inorganic salts.

Casein is classified as a pseudo-nucleo-albumin. The nucleo-proteins, so named because true nuclein may be obtained from them, are constituents of the cell nuclei, and differ in composition from ordinary proteins by containing from 0.5 to 1.6% of phosphorus. Casein from cow's milk contains, according to Hammarsten, 0.85% of phosphorus. It has been classified as a *pseudo*-nucleo-albumin because, upon digestion with pepsin, pseudo-nuclein rather than true nuclein is obtained.

Casein is practically insoluble in water, but dissolves readily in dilute alkaline solutions. Its precipitation as curd is dependent upon the presence of calcium salts.

Lactalbumin is the only other *protein* substance worthy of note in milk. This may be found in the filtrate after separating the casein. The total proteins contained in human milk average from 1.5 to 2.5 per cent while in cow's milk the proteins are 3.0 to 4.5 per cent. This difference, together with the variation of reaction and sugar-content, makes it necessary to "modify" cow's milk when it is used as an infant food.

The modification usually consists in the addition of lime-water (to change the reaction), of water (to reduce percentage of proteins), and of cream and milk-sugar (to increase fat and lactose).

The following table shows comparative composition:

	Reaction.	Total solids.	Proteins.	Sugar.	Fat.	Ash.
Human milk..	Alkaline	13.00%	2.70%	6.10%	4.00%	0.20%
Cow's milk...	Acid	14.00%	4.15%	4.90%	4.25%	0.70%

Fat. — The fat of milk exists as microscopic globules apparently inclosed in a protein-like membrane separating substance, the presence of which seems a necessary theory to account for the behavior of milk fat toward various solvents such as ether. The milk fat or butter fat consists largely of olein and palmitin with a slight amount of butyrin and traces of several other fatty acids.

Milk, as has already been stated, undergoes lactic acid fermentation readily and this may be induced by a considerable number of microörganisms. It is not, however, liable to alcoholic fermentation except under peculiar circumstances. Alcoholic fermentation may be induced by certain ferments, such as the Kephir grain used quite largely in the East, the product being known as Kumiss or milk wine. Kumiss originally was produced from mare's milk, but the name has also been applied to any milk which has undergone alcoholic fermentation.

FIG. 18. Milk and Colostrum.

Colostrum is a peculiar substance occurring at the very earliest stages of lactation. Its specific gravity is considerably higher than that of milk, being 1.040 to 1.060. It contains much more protein substance and is characterized by the presence of granular corpuscles known as colostrum corpuscles. (Fig. 18.)

DERIVED PROTEINS.

Meta-proteins — Acid Meta-protein. — The digestive action of the gastric juice on protein substances is the formation of an acid meta-protein, formerly called acid albuminate. The meta-proteins are characterized by the fact that they

are precipitated on neutralization and are not coagulated by heat. They may also be precipitated by saturation with common salt.

The Alkali Meta-protein or alkali albuminate is the stronger of these two classes of compounds when considered from a chemical standpoint; that is, the reactions are more marked, and some compounds will be formed with the alkali albuminate which are not produced when the acid albuminate is treated in a similar way. The acid meta-protein from the digestion of meat is known as syntonin.

The Proteoses (albumoses) may be considered as the next well-defined protein product of protein digestion following the albuminate. That is, leaving out the many intermediate products between which sharp lines of demarcation cannot be drawn, the decomposition of albumin brought about by enzymes or digestive ferments gives, first, acid albumin; second, albumose; and third, peptone. Albumose may be taken as a type of this second class of digestive products. Other proteoses, such as globulose, etc., are the substances derived from other proteins at a corresponding point of decomposition or peptic digestion. Albumose may be coagulated by heat at a temperature ranging upwards from 56° C., but, unlike albumin, as the temperature approaches the boiling-point the albumose goes again into solution, and at a boiling temperature may be separated from albumin by filtration. As the filtrate cools, albumose will again precipitate. The albumose is also precipitated by nitric acid, by ferrocyanide of potassium and acetic acid (the precipitate in both cases being dissolved by heat), and the other general protein precipitates. The biuret test gives a distinctive color with proteoses and peptones, it being a marked reddish shade rather than the violet or blue obtained with other proteins.

Peptones are the final products of *peptic* digestion of the proteins. They are soluble substances which give the biuret test similarly to the proteoses, but are not precipitated by heat,

by nitric acid, by potassium ferrocyanide and acetic acid, nor by saturation with ammonium sulphate.

Peptides. — The peptides are the simpler forms of the peptones, many of them being complex amino acids. Upon decomposition or hydrolytic splitting of peptide, the simpler amino acid, which is without the protein characteristics, results.

BLOOD AND MUSCLE.

Blood.

The blood, carrying oxygen and other forms of nutrition to all parts of the body, and returning carbon monoxide and the waste products of cellular activity, is an exceedingly complex substance. The composition of the blood itself, however, may be grossly described as a fluid (plasma) carrying in suspension the cellular constituents, red and white corpuscles. The plasma contains solid matter to the extent of about 8.9%. This is largely protein, consisting of serum globulin, serum albumin, a slight amount of nucleoprotein, and fibrinogen; also a fibrin ferment, thrombase or thrombin, by the action of which the fibrin is separated as a "clot" which mechanically carries down the corpuscles. As the clot contracts, the "serum" separates as a clear, amber-colored liquid, consisting of serum globulin (paraglobulin), serum albumin, and the fibrin ferment.

Fibrin. — The fibrin may be obtained free from corpuscles by whipping fresh blood. Under this treatment the fibrin separates as shreds, while the remaining fluid constitutes "defibrinated blood." The presence of lime-salts is essential to the coagulation of the blood, i.e., the decomposition of fibrinogen and separation of fibrin, in much the same way as in the decomposition of caseinogen and precipitation of casein from milk.

Fibrin, as usually obtained, is in the form of brown, stringy, and "fibrinous" masses, which are kept under glycerin for labor-

PLATE VII.—PHYSIOLOGICAL CHEMISTRY.
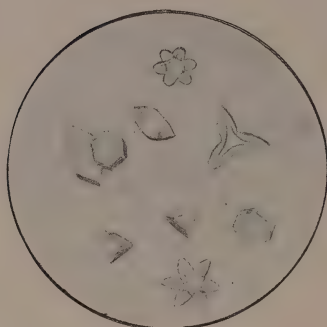
Fig. 1.
Edestin.
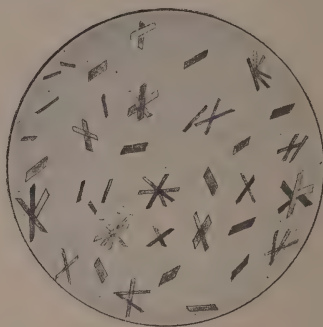
Fig. 2.
Teichmann's Hemin Crystals.
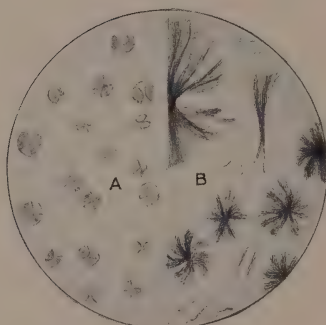
Fig. 3.—Fat Crystals.
A, Butter Crystals; *B*, Lard Crystals.
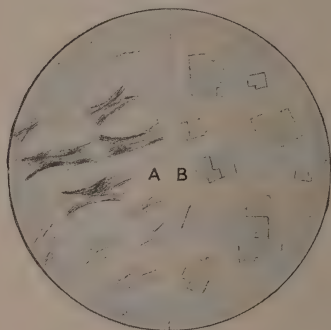
Fig. 4.
A, Fat Acid; *B*, Cholesterin.
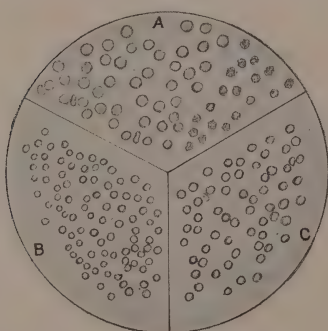
Fig. 5.
A, Human Blood; *B*, Horse Blood;
C, Dog Blood.
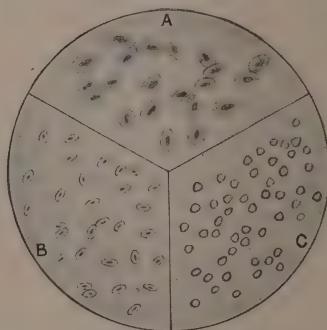
Fig. 6.
A, Frog Blood; *B*, Chicken Blood;
C, Fish Blood.

atory use. It is insoluble in water or alcohol. In dilute acid, (HCl), or alkali solutions, it swells and ultimately dissolves, although it may be several days before solution is effected. The fibrins from the blood of different animals differ in composition, as indicated by marked differences in solubility.

The chemistry of the red and white corpuscles is more complex and not so well known as the chemistry of the plasma, which we have considered. The red corpuscles consist of a frame of protoplasm, also called stroma, which contains lecithin, cholestrin, nucleoalbumin, and a globulin. (Hammarsten.) Upon and all through the stroma is the hemoglobin, which, together with its oxygen compound oxyhemoglobin, is responsible for the *color* of the blood. Oxyhemoglobin may be obtained as silky, transparent crystals of blood-red color.

From hemoglobin may be derived the blood pigment *hemochromogen*, containing iron, and this by oxidation is converted into hematin. The iron from the blood may, by decomposition of the pigment and subsequent combination with sulphur (FeS), cause discoloration of teeth. This is the theory of Dr. E. C. Kirk, and in the author's opinion is perfectly sound, and far more probable than other explanations which have been offered, but which do not recognize the formation of a sulphur compound.

The form of the red corpuscle is that of a biconcave disk without nucleus; by action of water it becomes swollen, and the hemoglobin may be washed away, leaving the "stroma." The diameter of the red corpuscles of human blood is about 1/3200 of an inch. Of the domestic animals, the corpuscles of the dog approach most nearly to the measurement of the human. The sheep, horse, and ox have smaller corpuscles than man, while those of birds, cold-blooded animals, and reptiles are larger (see Plate VII, Figs. 5 and 6).

The white corpuscles are rather larger than the red, and occur in much smaller numbers, a cubic millimeter containing

about 5,000,000 red to 7500 white. The white corpuscles present a much greater diversity of character than do the red. They contain one to four nuclei, and are capable of amœboid movements. The white corpuscles are also called leucocytes, aggregations of which constitute pus. The leucocytes are divided histologically into various classes, — lymphocyte, neutrophiles, eosinophiles, etc., — according as they are acted upon by different staining-fluids or fulfill some particular office; but these are not to be distinguished chemically.

Hemoglobin. — Hemoglobin may be separated from blood by shaking with a little ether and water and allowing to stand twelve hours on ice; or sometimes crystals may be obtained by simply allowing a drop of defibrinated blood to partially dry on a microscope slide. The hemoglobin from different animals crystallizes in more or less distinctive forms; for example, from human blood the crystals will be diamond shape or rectangular, from guinea pigs, tetrahedrons or octahedrons resembling the crystals of white arsenic, and from squirrels, six-sided plates.

The composition of hemoglobin has been given as 96% globin (a histone), and the remainder hemochromogen.

Hemoglobin forms compounds with various gaseous substances and furnishes a good example for the study of the law of mass action. In the lungs excess of oxygen slowly drives other gases, particularly carbon dioxide, out of combination, and forms oxyhemoglobin, while in the capillaries excess of carbon dioxide in venous blood replaces the oxygen. Hydrogen sulphide, nitric oxide, nitrous oxide, and carbon monoxide all form compounds with hemoglobin of various degrees of stability, the most stable being formed by carbon monoxide which acts by preventing the formation of oxyhemoglobin. Blood containing carbon monoxide hemoglobin is of a bright-red color, which darkens in the air much more slowly than ordinary blood.

Hematin is an oxidation product of hemoglobin and has been assigned the formula $C_{32}H_{32}N_4O_4Fe$.

Hemin, or Teichmann's hemin crystals, is the hydrochloric acid compound of hematin. (See Exp. 239, page 414, also Plate VII, Fig. 2.)

MUSCLE.

The chemistry of muscle is complex. It changes rapidly upon the death of the animal, so much so that the liquid which may be expressed from living muscle (or from muscle frozen immediately upon the death of the animal) has been called muscle plasma, in distinction from the fluid obtained in the same manner from dead muscle, which is called muscle serum. The chemical reactions of these solutions differ, due to the formation of sarcolactic acid in the dead muscle. The proteins differ in certain respects.

The two proteins of muscle plasma are given by Halliburton as paramyosinogen 25%, and myosinogen 75%. Of these the paramyosinogen seems to be a globulin, while the myosinogen, having many of the properties of a globulin, is soluble in pure water and is rather a mother protein from which the clot from muscle serum is produced. The protein of the muscle clot is known as myosin or myogen. Myosin may be precipitated from muscle serum by saturation with sodium chloride or magnesium sulphate. It has many of the properties of the globulins, but differs in the very important particular of not being precipitated by dialyzation. Among the more important extractive bodies obtained from muscle are creatin, carnin, inosite, glycogen, and lactic acid. Creatin is a xanthin body, being chemically a methyl-guanidin-acetic acid, which may appear in the urine as creatinin. (Creatinin is creatin minus water.)

Carnin is a white crystalline substance obtained from meat extract and converted by oxidation induced or produced by nitric acid, chlorine or bromine into hypoxanthin or sarkin. Its chemical constitution is not positively known.

Inosite, $C_6H_{12}O_6 + H_2O$, is a hexahydroxybenzene, $C_6H_6(OH)_6$ $+ H_2O$. It has a sweet taste, and was formerly erroneously classed with the carbohydrates. It is capable of yielding lactic and butyric acids (?).

Glycogen occurs in slight amounts in muscle, but decomposes after death, with formation of a reducing sugar. (Compare page 263.)

Lactic Acid is a constituent not only of muscle but also of various glands, of the bile, and of blood. For the chemistry of this substance, see page 222.

PART VII.

DIGESTION.

CHAPTER XXXIII.

SALIVA PROPERTIES AND CONSTITUENTS.

The saliva is a mixed secretion from the parotid, submaxillary, and sublingual glands, together with a slight amount obtained from the smaller buccal glands. The chemical composition of the secretion from these various sources differs considerably, but from a dental standpoint we are much more interested in the mixed saliva and its constituents than the differences in the products of the various glands. The notable differences are that the mucin is practically wanting in the parotid saliva. The alkaline salts seem to be in smaller proportion in the parotid saliva than in the other two. Potassium sulphocyanate is a constituent of all varieties of saliva, although more constantly present in the submaxillary and in the sublingual than in the parotid. The parotid, on the other hand, contains a larger proportion of dissolved gases. The data on the composition of these varieties differ to a considerable extent and comparisons are not wholly satisfactory.

The mixed saliva contains, according to Professor Michaels, all the salts of the blood which are dialyzable through the salivary glands, and hence furnishes a reliable index of metabolic processes which are being carried on within the system. In order for this fact to be of practical value, two things are obviously of prime importance: First, methods of analysis which are not too complicated and which are at the same time conclusive;

second, a knowledge regarding the source of the various con-
stituents found which will enable us to make a rational inter-
pretation of the results obtained.   In both of these fundamentals
we are very much hampered by lack of knowledge; as yet there
is much to be desired in the way of practical clinical tests for
the various salivary constituents, and very much to be learned
as to their meanings in order to make deductions which shall
be conclusive. We are led to believe from the work of an
increasing number of specialists that this subject of salivary
analysis promises much and is certainly worthy of careful
investigation.

The *quantity* of saliva secreted in twenty-four hours is vari-
ously estimated from a few hundred to 1500 c.c.; 1200 to 1500
is the more probable amount. The quantity is diminished in
fevers, severe diarrhea, diabetes, and nephritis, by fear and
anxiety, and by the use of atropine.   It is increased by smoking,
by mastication, by the use of mercury, potassium iodide, or
pilocarpin.   The flow of saliva is also increased by action of the
sympathetic nervous system, during pregnancy, and by local
inflammatory process.

Physical Properties. — The physical properties of saliva in-
clude its appearance, specific gravity, reaction, color, and odor.

Appearance. — The appearance is clear, opalescent, frothy,
or cloudy; normal saliva is usually opalescent.   It may become
turbid by precipitation of lime-salts caused by the escape of
carbon dioxide.

Specific Gravity. — Specific gravity ranges from 1.002 to 1.009,
the total solids being only from 0.6 to 2.5 per cent.

Reaction. — The reaction is normally alkaline to litmus-
paper or to lacmoid. Normal saliva, however, fails to give
an alkaline reaction with phenolphthalein, due to the presence
of free carbon dioxide, which may be present to the extent of
nineteen parts in a hundred, by volume. If the sample be
subjected to even a slight degree of heat the acid gas is expelled;

then the usual pink color may be obtained with this indicator. Saliva may be acid upon fasting, particularly before breakfast and also after much talking. Acid conditions may exist which are local in their character and due to lactic acid fermentation. Acid salivas may also be met with in cases of rheumatism, mercury salivation, and diabetes. By exercise of the glands, as during the chewing of food, the alkalinity is increased; oftentimes the reaction changes from faintly acid to alkaline during this process, the proportion of alkaline salts becoming greater, although the total solids as a whole are slightly diminished. This fact of the change in the reaction from acid to alkaline has been explained by ascribing the acidity to fermenting particles in the mouth; the continued process of chewing and swallowing washes this away, or, in other words, the change in reaction is a mechanical one rather than a change of the chemical composition of the secretion. This explanation seems to be a superficial one and without sufficient experimental foundation.

The acidity of saliva, as indicated at the bottom of page 292, is referred to the behavior of the saliva to phenolphthalein, and is in large part due to the presence of free carbon dioxide.

The sources of carbon dioxide in saliva are probably three: carbon dioxide dialyzed through the salivary glands, traces from carbohydrate fermentation, and more or less absorbed from contact with expired air.

The saliva obtained by chewing paraffin (a process calculated to furnish the maximum amount from the last two sources), may yield several times the amount of free carbon dioxide that another sample taken from the same patient by a saliva ejector will give.

Acidity of saliva may be temporary when it may be entirely removed by drawing air through the heated (not boiled) sample. The permanent acidity may be determined by titration of the sample after removal of carbon dioxide.

The apparatus pictured in Fig. 19 has been used by the author for this acidity determination.

The air is drawn from left to right first through a potash bulb (*A*) to absorb atmospheric carbon dioxide, next through
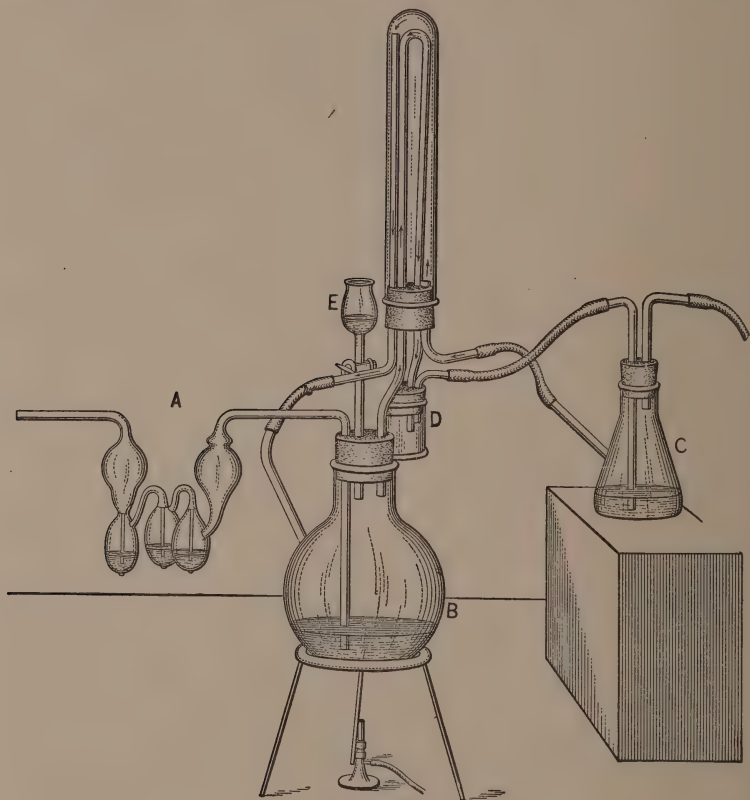
FIG. 19.

10 c.c. of saliva diluted with 20 c.c. of water contained in a small Soxhlet flask (*B*) whereby the carbon dioxide from the saliva is carried through the " test-tube " condenser and collected in baryta water in the Erlenmeyer flask (*C*) at the left. This in turn is connected with a suction pump or aspirator.

The " drip cup " (D) has been found necessary when working with very viscid samples. The thistle tube (E) holds water for maintaining the volume in (B) if the condenser is not used.
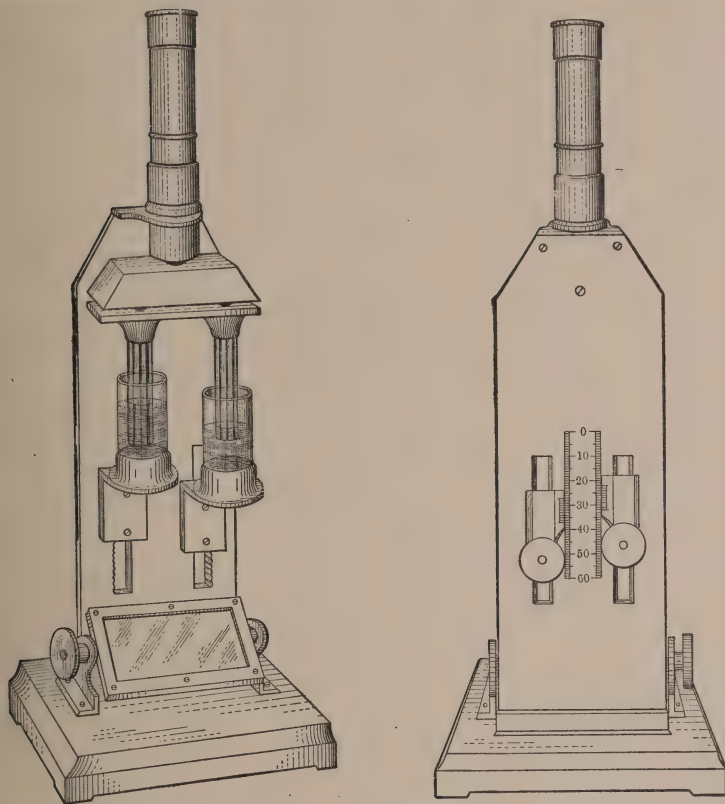
Fig. 20. Colorimeter.

The amount of free carbon dioxide may be determined by adding a standard carbonate solution ($N/100$ Na_2CO_3) to a volume of baryta water equal to that used in the Erlenmeyer flask and then comparing the degree of turbidity obtained. This may be done by viewing through flat-bottom tubes (shell

tubes) of about 20 c.c. capacity, or, in many cases, better, by use of the Duboscq colorimeter used for determination of ammonia (Fig. 20, page 295), or better still by the use of the nephelometer made with the Duboscq colorimeter after the method of Dr. Bloor. (Journal of Biological Chemistry, vol. 22, p. 145, 1915.) This apparatus may also be used to advantage in the determination of calcium in saliva, or acetone bodies in urine. The nephelometer differs from the Duboscq colorimeter in that it makes use of reflected rather than transmitted light.

The following method for the determination of temporary acidity is also recommended. Force air free from carbon dioxide through a measured volume of saliva (20 c.c.) which has been previously mixed with an equal volume of water, then into baryta-water containing a little barium chloride, using a Folin absorption tube (Fig. 25, page 310). The carbon dioxide thus becomes fixed as barium carbonate. Transfer the precipitated carbonate to a filter paper and wash free from chlorine. Dissolve off paper in dilute hydrochloric acid, collecting filtrate in porcelain dish. Evaporate to dryness over water bath and titrate chlorine with $N/20$ silver nitrate. 1 c.c. $N/20$ $AgNO_3$ = .0010917 gram of CO_2.

Another method consists in passing carbon dioxide as above, into a measured volume of standardized baryta-water ($N/20$) and titrating excess of barium hydroxide with $N/20$ oxalic acid. The end point is determined by "spotting" onto fresh tumeric paper. When the paper ceases to turn brown-red the end of the reaction has been reached.

Permanent acidity is of comparatively rare occurrence and is due either to the presence of acid salts, such as NaH_2PO_4, or slight amount of organic acids possibly combined as acid metaprotein. This acidity and its clinical significance is at present under investigation.

Color. — Saliva is usually colorless when fresh, but upon

standing for twenty-four hours may assume various tints, which are developed from constituents derived from bile. (Professor Michaels.) Saliva may be colored red or brown by the presence of blood or blood pigments, but in such cases the source of the color is usually local and easily discovered.

Odor. — Normal saliva is practically odorless. In cases of pyorrhea there is usually a peculiar fetid odor easily recognized. In other pathogenic conditions the odor may be slightly ammoniacal, or occasionally resemble the odor of acetone or garlic.

Constituents. — We should here distinguish carefully between saliva proper and sputum. The constituents of sputum are derived from the air-passages rather than from the salivary glands, and are not at present under consideration. Among the *normal* constituents of saliva are included mucin, albumin, ptyalin, also oxidizing enzymes, ammonium salts, nitrites, potassium sulphocyanate, alkaline phosphates, and chlorides, with traces of carbonates; and, in the sediment, epithelium cells, occasional leucocytes, and fat globules. The *abnormal* constituents wi l include glycogen, urea, dextrin, rarely sugar, cholesterin, derivatives from bile, lecithin, xanthin bodies or alkaline urates, acetone, lactic acid, and crystalline elements resulting from insufficient oxidation or perverted glandular function. These latter are recognizable by the micropolariscope. Mercury and lead may also be found in saliva in cases of poisoning by salts of these metals.

Mucin. — The secretion from the parotid gland contains practically no mucin, but the sublingual saliva contains large amounts. Mucin is, according to Simon, the most important constituent of the saliva, not excepting ptyalin. The various glands contributing salivary mucin do not in all probability furnish just the same kind of protein; moreover, the mucin from different individuals seems to vary in composition and properties, some yielding more abundant acid decomposition

products than others (see article by W. D. Miller, in Dental Cosmos for November, 1905), while, according to Professor Michaels, the mucin varies much in the same individual in health and disease. The changes in the characteristics of salivary mucin have been studied but little, and the investigation of these changes, as indications of diathetic states, promises much.

An excess of mucin in the saliva tends to an increase of bacterial growth, from the fact that it furnishes increased facilities for multiplication; it has been suggested that it may also give rise to mucic acid, and thereby be a possible factor in tooth erosion. (Dr. G. W. Cook in Dental Review, May, 1906, page 461.)

Albumin. — Albumin is present in very small quantities, increased during mercurial ptyalism, usually in cases of pyorrhea, and, according to some authorities, in various albuminurias. It may be detected by usual methods after the separation of mucin.

" According to Vulpian, the quantity of albumin is increased in the saliva of albuminurics of Bright's disease. The saliva of a patient with parenchymatous nephritis had mucin 0.253 and albumin 0.182 per cent. The saliva of another patient, with albuminuria of cardiac origin, contained mucin 0.45, albumin 0.145 per cent. In a healthy man there was found mucin 0.320, albumin 0.05 per cent. This fact has been confirmed by Pouchet, who found these substances in greater quantities." *

Ptyalin. — Ptyalin is the principal ferment of the saliva; it converts starch, by hydrolysis through the various dextrins (page 263), to maltose. The maltose in turn is converted into glucose by a second ferment, known as maltase, which exists in saliva in very small quantities.

* Dr. Joseph P. Michaels. S. S. White's reprint of paper read before International Dental Congress, Paris, 1900.

The activity of ptyalin is greatest at a temperature of 40° C. Very faintly acid saliva is the best media. Neutral and faintly alkaline salivas are next in order.

The amylolytic power of a given sample of saliva may be determined by the action on dilute starch paste. In making comparative tests it is essential that the conditions under which the ptyalin is allowed to act should be exactly the same, especially as regards the temperature and duration of the process. A slight variation in the strength of the starch solution is of no consequence, as starch is supposed to be in excess. (See Exp. 245 on page 416, also method on page 313.)

Proteolytic Enzymes. — Upon incubation with certain products of protein digestion (dipeptides) proteolytic action of saliva has been noted; whether this action is due to an enzyme or to bacteria is an open question. (See fifth edition of Hawk's Physiological Chemistry, pages 57 and 58.)

Oxidases. — As a result of the work of Dr. C. F. MacDonald in the author's laboratory, the following conclusions were reached regarding these enzymes:

First. That human mixed saliva contains an oxidizing enzyme distinct from ptyalin.

Second. That the enzyme exhibits the properties of both an oxydase and a peroxydase.

Third. That it is a product of the body (probably glandular) metabolism and may be increased in quantity, or activity by mastication.

Fourth. That it is more resistant to heat than ptyalin, but more easily destroyed by acids.

Fifth. That the color obtained with a freshly prepared 1% solution of pyrocatechol is sufficient test for this enzyme in saliva.

The test for oxidizing enzymes may be made with the pyrocatechol as given on page 314; also by the use of phenolphthalin

(reduced phenolphthalein). This last reagent has recently been rendered available by the work of Dr. H. L. Amoss, Harvard Medical School, who has given us a concise and simple method for its preparation. (Jour. Biolog. Chem., 1912.)

Phosphates and Carbonates. — These salts are probably present in both acid and neutral forms; that is, the phosphate may exist as Na_2HPO_4 also as NaH_2PO_4, and at times both of these may be present at once. The acid carbonate, $NaHCO_3$, is an undoubted constituent, while the neutral carbonate is probably not present at all. Chittenden says that mixed human saliva contains normally no sodium carbonate whatever.

As explained by Dr. Kirk, the normal reaction by which overacidity of the blood is taken care of by renal epithelium is $H_2CO_3 + Na_2HPO_4 = NaH_2PO_4 + NaHCO_3$, and when conditions are such as to produce larger quantities of carbonic acid than the kidneys can eliminate in accordance with the above reaction, there is an increased acidity of the saliva as well as of the urine.* In the hypoacid individual, the so-called alkaline sodium phosphate, Na_2HPO_4, is present in the greater quantity. In diabetic patients, sugar has very rarely been found in the saliva; one case coming under the observation of the author was that of a woman of middle age, with diabetes of long standing, with 8% of sugar in the urine, and from this case there were obtained a very few osazone crystals by subjecting a considerable quantity of saliva, after concentration, to the phenylhydrazine test.

Urea has been repeatedly found in the saliva of patients suffering from chronic nephritis.

Acetone is of quite frequent occurrence in the saliva. In diabetic patients this substance is often present in comparatively large amounts, sometimes sufficient for the detection of the acetone by its characteristic odor. Acetone may appear in the saliva when it is not present in the urine. In such cases it

* International Dental Journal, February, 1904.

has usually resulted from disordered digestion and a consequent faulty metabolism. (For further consideration of acetone, see Urine.)

Cholesterin and lecithin have been found by Professor Michaels in pathological saliva, and leucin has been found by Michaels in a case of lupus and, according to Novey, in a case of hysteria.

Of the crystalline salts which may be separated by evaporation of dialyzed saliva, the sodium oxalate and the lactates and acid lactates of lime and magnesia are of the most importance and have been the most thoroughly studied. As these salts may likewise be separated from urine their significance will be studied under that head.

Ammonium Salts. — Ammonium salts occur chiefly as chloride, probably to some extent as sulphocyanate, and occasionally as oxalate. Professor Michaels says that ammonia must be considered as a more completely oxidized form of nitrogen than urea; hence its relative increase is observed in all diseases which occasion an excess of nitrogen and urea, as in tuberculosis and all hypoacid diatheses. There is a decrease of ammonia whenever the nitrogen fails to reach the stage of oxidation represented by urea. This condition is accompanied by uric acid and other products of deficient oxidation, and characterizes the hyperacid state.

While these statements are consistent with Dr. Michaels' conception of the hyper- and hypo-acid diatheses, the student is not to understand that ammonia is really an oxidation product, for we have already seen that it is formed by the splitting of protein derivatives. Characteristic crystals of ammonium chloride may be found by microscopical examination of the residue obtained by evaporating a clear drop of almost any saliva. (Plate VIII, Fig. 1, page 316.)

Potassium Thiocyanate represents the salts of HCNS found in saliva. It occurs only in very slight traces in other body

fluids, and in saliva only to the extent of 0.001 to 0.02%. Dr. Michaels considered the proportion of thiocyanates relative to the ammonia to be of importance and states that in health the ammonium salts and the thiocyanates are present in very slight amounts, and the color-tests, with Nessler's solution and with ferric chloride, respectively, are of about equal intensity. In the hyperacid state the sulphocyanates are in excess of ammonia, while in hypoacid conditions, the ammonia exists in the greater quantity. Sulphocyanate is detected by means of ferric chloride, and distinguished from meconates and acetates, as indicated by Exp. 247, page 417.

As we shall see in a subsequent chapter the intensity of color produced by ferric chloride and thiocyanate is not necessarily an index of the quantity of HCNS present, hence the above conclusions are of questionable value.

The sulphocyanates are normal constituents of saliva, and consequently always present. According to A. Mayer (Deutsch. arch. f. klin. med., Vol. 79, No. 394), the sulphocyanates, without doubt, result from the decomposition of proteins, and exist in the urine in quantities variously estimated from twenty to eighty milligrams per liter, while in saliva it has been estimated from sixty to one hundred milligrams per liter. Professor Ludholz of the University of Pennsylvania says that the sulphocyanates are eliminated in increased amounts in conditions where there is a lack of oxygen in the system, thus corroborating statements of Professor Michaels (see Ammonia). Dr. Fenwick (Lancet, 1877, Vol. II, page 303) demonstrated that the quantity of KCNS was directly dependent upon the bile salts in the blood. He found an increase of the salt in liver disorders attended with increase of bile salts in the blood, and marked increase in jaundice. In gout, rheumatism, and conditions producing pyorrhea, it is also claimed to be present in considerable quantity.

The sulphocyanates are usually present in more than normal

quantity in the saliva of people addicted to smoking tobacco.*
The claim has been made for this salt that it exerts a specific
antiseptic action toward bacteria.

While the sulphocyanates, or, in fact, any salt in sufficient
concentration, will have an inhibitory action on the growth of
bacteria, it is rather doubtful if this is the particular office of
KCyS in the saliva.

Nitrites. — That nitrites exist in most salivas is without ques-
tion. So far as we know at present, the nitrites are apparently
incidental, and occur as intermediate products in the oxidation
of ammonia to nitrates, just as they do otherwise in nature out-
side of the animal body.

It is not at all improbable that the proportion of nitrates is
dependent upon activities of the oxidases. This has, in some
cases at least, been proven to be the case, as the same sample
of saliva has frequently given steadily diminishing quantities
of nitrites until they have wholly disappeared in cases contain-
ing active oxidizing enzymes.

Nitrates occur in the saliva but so far as known are without
clinical significance.

* See article by Dr. J. Morgan Howe in Jour. of the Allied Societies, Vol. 4,
p. 183.

CHAPTER XXXIV.

ANALYSIS OF SALIVA.

THE analysis of saliva may be taken up from two distinct standpoints, and considering our present lack of positive knowledge on this subject it may for a while be expedient so to study it. First, we will study a few tests of saliva of such a character that they may be made with simple apparatus, and which might be used by any dental practitioner with sufficient time and interest, to contribute to our general knowledge; secondly, we may study saliva by accurate laboratory methods which are not available for general use, but which are necessary for the establishment of positive data, and in fact necessary for an intelligent schedule of tests under division one.

In 1911 and for one or two years previous the National Association made an effort to establish uniform methods of salivary analysis, and it is deeply to be regretted that this effort was not continued until a system of examination had been perfected which might have become a recognized one for all workers along these lines. A necessity of uniform methods is generally recognized by other classes of chemists but as yet the fact remains that the dental chemist is obliged to formulate his own analytical schemes.

We shall make three divisions of the methods to be used. Methods marked I are in part taken from Professor Michaels and are the simplest ones applicable to small amounts. They will give results of varying degrees of accuracy, but are of value because of the ease and rapidity with which they may be used.

Methods marked II are retained from Dr. Ferris' report to the National Dental Association at its annual meeting in 1911,

and reported in the Dental Cosmos for November of that same year, on pages 1295, etc.

Methods marked III are those which the author believes to be the most accurate and the most satisfactory in exhaustive determinations.

Physical properties of the saliva should first be noted. In method I, the color and appearance of the perfectly fresh sample is to be carefully compared with the appearance and color after standing for forty-eight hours in a small, tightly covered vial. The color may be yellowish, greenish, or brown, according to the variety of the derivative of biliverdin from which the color is obtained.* The general appearance may also change independently of any color. A saliva that is, when fresh, hypoacid in character, is, after forty-eight hours, usually markedly opalescent and of offensive odor, while a hyperacid saliva may have become clear or cloudy but without odor.

By method II, we should add to this examination a viscosity test which will be of value as indicating the amount of mucin, as probably the mucin content affects the viscosity more than any one constituent.

The **viscosity** may be determined by use of the apparatus pictured in Fig. 21 (page 306).

The essential features of the viscosimeter are a straight graduated tube with the *constriction* (*C*) jacketed so that the conditions under which a given sample will pass through the opening will always be under absolute control.

The apparatus is standardized by partly filling with distilled water in which the bulb of a thermometer is immersed.

The temperature of the distilled water is brought to 25° C. The thermometer is removed to facilitate reading and from 5 to 10 c.c. of the liquid are allowed to run out, the time consumed being accurately determined by a stop watch.

* Dr. Joseph P. Michaels. S. S. White's reprint of paper read before International Dental Congress, Paris, 1900.
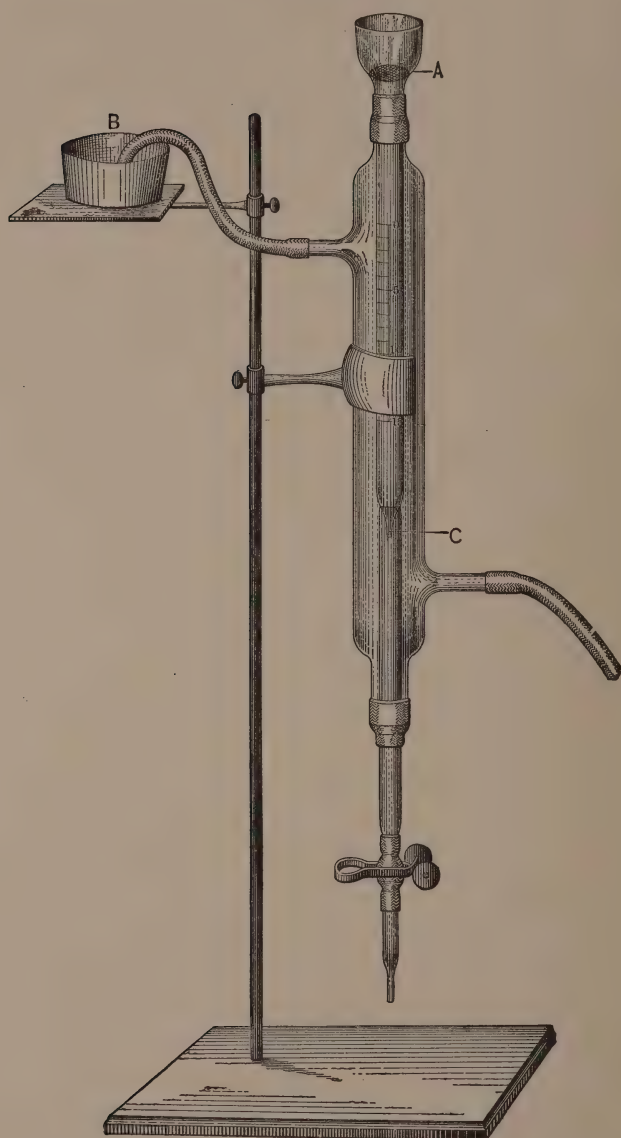
FIG. 21.

The viscosity of saliva is determined in the same way, care being taken that only a perfectly clear solution is used as fine particles will clog the opening at C. The use of the stop cork as pictured in Fig. 21 is undesirable, in fact it has been found that straining the saliva, filtering through paper or even centrifugalizing in order to separate the solid portions will occasion a variation in the results obtained. The first determination should be carefully made and used, as repeated determinations result in a regular diminution of the viscosity figure due to mechanical changes brought about by passing the saliva through the very small opening at C.

If the constriction of the graduated tube is sufficiently great, i.e., the opening sufficiently small, comparison may be made by counting drops delivered in a given time. This is not advised, as there is much greater difficulty in obtaining the saliva free enough from suspended particles so as not to clog the tube.

The inner tube should always be filled to the same mark in the determination as that used in the standardization of the instrument.

The **reaction** may be taken in method I by the simple use of litmus paper. This test has a general value, and is sufficient to detect extreme conditions. Our second method should be a quantitative one, and the degree of alkalinity should be determined by indirect titration. Add excess of $N/100$ HCl to 10 c.c. of sample, and titrate back to yellow color with $N/100$

FIG. 22. — Pyknometer.

NH_4OH. Use paranitrophenol as indicator. The degree of acidity, using $N/100$ alkali and neutral phenolphthalein as an indicator, should be determined next. Then the reaction, after driving off carbon dioxide, should be ascertained. The per-

manent acidity, if such exists, should be found a useful factor in the study of Dental Caries and may be determined by the apparatus pictured on page 294.
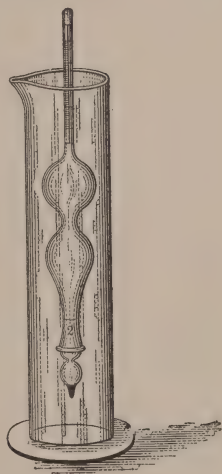
Specific Gravity may be taken (Method I) by an ordinary urinometer or a specific gravity bulb if the quantity is sufficient, the reading to be made from beneath the surface of the liquid. If the quantity of the saliva is small, it may be diluted with an equal volume of water, and the last two figures multiplied by two will give the gravity of the undiluted sample, or the gravity may be taken

FIG. 23.

by the pyknometer in which the bulb of the instrument is filled with saliva accurately to the mark *M* (Fig. 22), and then the reading of course on this instrument will be from the bottom up, and the lower the bulb sinks the greater will be the gravity of the sample. This method, devised by S. A. De Santos Saxe, M. D., for use in examination of urine, has been suggested by Dr. Ferris and adopted by the National Dental Association as an official method.

For very accurate work the use of specific gravity bottles is recommended. These may be obtained holding one, two, and five cubic centimeters (Fig. 23), and with an accurate balance of course the gravity can be accurately obtained.

Thiocyanate (Sulphocyanate) **Tests.** — (Method I.) To a large drop of saliva on a white porcelain surface, add about

FIG. 24. — Sulphocyanate Tubes.

half as much 5% ferric chloride, acidified with hydrochloric acid. A reddish coloration indicates the presence of thiocya-

nate. "(Method II.) Use a colorimetric scale (Ferris and Schradieck), place 1 c.c. of the specimen in tube *A*; 1 c.c. of 1/2000 ammonia sulphocyanate in tube *B* (Fig. 24); add two drops of a 5% ferric chloride solution to each tube, add aqua distillata in tube *B*, until its color matches that of the specimen. Read the scale in thousandths and ten thousandths.

" Care must be taken to have the bottom of the meniscus on the line. If these tubes are introduced in the colorimeter, the readings can be made more accurately. If, later, diacetic acid ester or other substances giving similar color with ferric chloride are found, a correction is made in the finding."

With an excess of ferric chloride this test gives an idea of whether the amount of thiocyanate is much or little, but the careful dilution of a sample and comparison with standard has been found to be practically valueless for small amounts, which fact may be explained by the following experiment.

If ferric chloride and potassium thiocyanate are mixed in molar proportions and diluted one to one thousand with distilled water a solution results which is within the lower limits of the thiocyanate content of the saliva, but it also happens that ferric thiocyanate of this strength dissociates so that 10 c.c. in a 25 c.c. cylinder will have only a very pale straw color (the undissociated $Fe(CNS)_3$ *only* is red).

If a drop of $FeCl_3$ solution (M/1) is added the reddish color is restored, the ferric chloride being in excess, but the addition of 5 c.c. of saliva containing the average amount of thiocyanate instead of increasing the color on account of the additional $Fe(CNS)_3$ produced, causes the color to become much paler than if 5 c.c. of distilled water had been added. The explanation is obvious. The total amount of ferric thiocyanate produced, while still within the limits of the salivary content, is not concentrated enough but what the proportion of ionized salt is still in excess, and further the added saliva has con-

tributed a certain amount of KCl which will reduce the color by inducing the reverse reaction.

$$3 \, KCl + Fe(CNS)_3 = FeCl_3 + 3 \, KCNS.$$
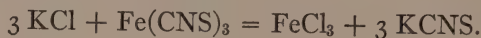
Addition of either the acid or alkaline sodium phosphates (both probable constituents of saliva) will also decrease the intensity of the color, so in order to make accurate comparisons of very dilute solutions it is necessary to know the amounts of ionizable salts in the sample, which is impracticable.

Ammonium Salts. — (Method I.) To a drop of saliva add one drop of Nessler's reagent: a yellow to brown color shows the presence of ammonium salts. If a precipitate forms by the addition of Nessler's reagent, it indicates either a large amount of ammonia or the presence of urobilin. If due to urobilin the precipitate is of a rose color after desiccation. Ammonium salts are usually seen in the evaporated drop examined by polarized light. (Plate VIII, Fig. 1.)

(Method III.) A modification of Dr. Folin's ammonia test in urine, using the Duboscq colorimeter.

Measure out 10 c.c. of saliva in a large Jena test-tube. Add 2 c.c. of a solution containing (a) potassium oxalate, (b) potassium carbonate (15% of each).

FIG. 25.　By means of an air current, drive the ammonia through a Folin absorption-tube (Fig. 25) into a 100 c.c. wide-mouth bottle containing 2 c.c. N/10 HCl, and about 30 c.c. water. In twenty minutes, all the ammonia should have gone over.

Remove the delivery-tube, rinsing it with water, and transfer contents of bottle to 100 c.c. measuring flask, rinsing with sufficient water to make total volume about 60 c.c.

Pipette out 1 c.c. of standard ammonium sulphate into another 100 c.c. measuring flask and dilute with water to about 60 c.c.

Nesslerize both solutions simultaneously in the following manner. Provide two small beakers (100 c.c.) and place from 10 to 15 c.c. of distilled water in each. Add to each 5 c.c. of Nessler's reagent. Mix the reagent with water, and add immediately to the ammonia solutions. Add about one-third of the diluted Nessler reagent at a time, and shake after each addition.

Fill both flasks up to mark with distilled water, mix and compare the colors by means of a Duboscq colorimeter (Fig. 20, page 295).

Urea. — Reagent, sodium hypobromite as used for urea in urine analysis (Appendix, page 427).

Fill the tube of a Ferris modified Doremus ureometer with a saturated salt solution. Close the stopper, and add 1 c.c. of saliva to the upper tube. Allow this to run through the stopper carefully, then close, and add 1 c.c. of the reagent. When this has gone through, close the stopper quickly, set up the apparatus, and allow to stand one hour or longer. Then, by gently tapping, cause any bubbles adhering to the sides of the tube to rise to the top, and read the amount of gas collected. Each division represents 0.025.

Chlorides. — (Method I.) To a drop of saliva add a small drop of a 5% solution of neutral chromate of potassium, K_2CrO_4. Mix with a glass rod and add one drop of a 1/10% solution of silver nitrate. This constitutes the test for chlorine, which, if present in normal quantities, will give a reddish precipitate, gradually becoming white. Should the precipitate remain red it shows the chlorine deficient or less than normal in amount. If the precipitate rapidly turns white, or if a white precipitate is formed to the exclusion of the red, chlorine is increased in amount. High chlorine is indicative of hypoacid diathesis.

(Method II.) To 1 c.c. of the specimen add 4 c.c. of distilled water and two or three drops of potassium chromate; then titrate with N/40 silver nitrate solution, until the first appear-

ance of a permanent reddish tinge. Multiply the number of cubic centimeters of nitrate used by 0.0886 to find the amount of chlorine in 100 c.c. of saliva.

(Method III.) Proceed as in Method II except that it is recommended to use 5 c.c. of the specimen and N/20 silver nitrate solution. Then the number of cubic centimeters of silver solution used multiplied by 0.00177 will give the weight of chlorine in the 5 c.c. of saliva taken. This times twenty will give the amount in 100 c.c. or the per cent.

Glycogen. — (Method I.) A drop of saliva may be tested for glycogen by the addition of one drop of an aqueous solution of iodine and potassium iodide. This must be left for some time, as the test is not obtained until the drop is dried; then, if the color is a feeble violet around the edge, glycogen is indicated. If the color is a strong brown-red it indicates erythrodexterin, if gray or black a reducing sugar.

Phosphates. — The phosphates in saliva are determined as in urine except that it is necessary to modify the process slightly as given on page 340.

Calcium may be determined by the following volumetric method recommended by Dr. Percy R. Howe, Dental Cosmos, April, 1912. To 5 c.c. of saliva, add as much more distilled water and a slight excess of oxalic acid or ammonium oxalate (5 c.c. of normal solution will be sufficient). Add ammonium water to alkaline reaction, heat nearly to the boiling-point, and allow to stand for 20 to 30 minutes. Filter through a hardened filter paper into a small beaker which is allowed to stand on a piece of black glazed paper. Under these circumstances, a slight rotary motion of the beaker will show if any of the white precipitate of calcium oxalate is passing through the paper.

After filtration is complete, wash five times in hot distilled water; then place the precipitate, together with the paper, into a small beaker, add about 30 c.c. of dilute sulphuric acid, and

heat nearly to the boiling-point; then titrate with N/20 permanganate solution.

Acetone. — (Methods I and III.)   In the fifth drop dissolve a small crystal of potassium carbonate, then add a drop of Gram's reagent, when a marked odor of iodoform will indicate the presence of acetone.   Should this odor be obtained, it is better to repeat this test upon a microscope slide, and examine carefully for the characteristic hexagonal crystals of iodoform (Plate V, Fig. 1, page 204).

Nitrites. — (Method I.)   Nitrites may be detected by adding to a large drop of saliva on porcelain a few drops of freshly prepared reagent, made by dissolving a very little naphthylamine chloride and an equal amount of sulphanilic acid in distilled water strongly acidulated with acetic acid.   A purple coloration is a test for nitrates.

This method could be made quantitative in a manner similar to the colorimetric methods for ammonia, or thiocyanate of potassium; but, at the time of the present writing, there seems to be no particular reason for this amount of work.

Amylolytic Enzymes. — (Method II.)*   Preparation of starch paste.   Put 15 c.c. of distilled water to boil.   Meanwhile, weigh out three grams sterile starch and mix with 6 c.c. cold distilled water.   Add drop by drop under constant stirring to the boiling water, then rinse out with 5 c.c. of distilled water any particles of starch adhering to the dish and add to the boiling starch solution.   Boil one minute under constant stirring.   Cool to blood temperature and add gradually 4 c.c. of N/100 iodine solution.

This makes 30 c.c. of a 10% starch solution, which, when colored, is of a dark blue, and can be kept several days in the ice-box.

Filling the Tubes. — Suck up the paste into glass tubes of 1.5 mm. diameter, and cool in the ice-box.   Just before using,

---

* Method II as usual by Dr. Ferris (see page 304).

make a file mark 1 cm. from the end of the tube and break off the piece of tubing so that it is full of the blue starch paste. Be sure that this small tube is broken so as to leave each end square and full of paste. Examine under low-power microscope.

Determination of Enzyme. — Immediately after delivery of the specimen, measure 2 c.c. of saliva into a test-tube. Place it in the small tube of starch paste, and heat the whole in a thermostat at from 37° to 38° C. for half an hour. The enzyme of the saliva will dissolve the paste from the ends of the tube, leaving a blue column of paste unchanged in the center of the glass tube. After half an hour, measure with a micrometer gauge the total length of the tube and the length of the blue starch paste column remaining undissolved. The difference between these two measurements represents the amount of starch digested by the enzyme. Since the quantity of ferment in any fluid varies with the square of the length of the column digested, the quantity of ferment in the saliva is found by squaring this difference. Multiply by 100 to give the enzymic index.

Oxidizing Enzyme. — (Oxydase.) Methods I and III consist of treating 5 c.c. of saliva, diluted with an equal volume of water, with about 1 c.c. of a 1% solution of pyrocatechol. The color obtained is a characteristic brown, developing within thirty minutes.

Mucin and Albumin. — (Method I.) *Mucin* may be separated after taking the gravity by the addition of a little acetic acid. It should then be filtered off, but it will be necessary to dilute and agitate, in order that a fairly clear filtrate may be obtained.

Albumin may be demonstrated in the filtrate, from which mucin has been separated by underlaying with strong nitric acid. This is Heller's test for albumin in the urine, and is best performed in a small wine-glass with round bottom and plain sides.

Total Solids and Ash. — (Method II.) These should be determined immediately upon the arrival of the specimen to avoid error through evaporation of moisture.

Use a platinum or fused silica dish of constant weight which has been kept in a desiccator over sulphuric acid. Weigh the dish accurately and rapidly, then introduce $2\frac{1}{2}$ c.c. of the well-mixed specimen and heat in a drying oven, not over 100° C., for two hours. Then place in the desiccator over sulphuric acid for twelve hours or longer, and weigh accurately and rapidly.

The difference between these weights represents the weight of total solids. To calculate the percentage, divide by two and one-half times the specific gravity.

Add to the dish two or three drops of fuming nitric acid, and heat over a flame, keeping the dish two inches above the top of the flame, until the black color has become white. Heat in the direct flame until glowing, place at once in desiccator to cool for one or more hours, and weigh. Calculate the percentage of ash in same manner as of total solids.

(Method III.) Total solids and ash are best obtained as follows: evaporate over a water bath five grams of the sample thoroughly mixed with a weighed amount (half a gram) of ignited magnesium oxide. The weight of residue (less the magnesia) obtained by drying at 100° C., gives the total solids. These may be ignited until white ash is obtained and again weighed. The second weight (less magnesia) gives the ash.

The use of the magnesium oxide serves to retain carbonates and chlorides in the total solids and the chlorides in the ash. It also obviates the necessity of oxidation with nitric acid, which would decompose many of the inorganic constituents of the ash.

To determine weight of sediment obtain total solids as above; then if a portion of the saliva is carefully filtered and the solids determined in the clear filtrate by the same method, the difference between the two determinations of solids will be the weight of sediment, epithelium, leucocytes, etc.

CRYSTALS FROM THE DIALYZED SALIVA.

To obtain characteristic crystals, as has been explained in considering the subject of micro-chemistry, uniformity as to conditions under which the crystallization takes place is a necessity. In the case of saliva, however, we are not producing new compounds, but simply searching for compounds already formed and existing in unknown proportions in the samples tested. It is therefore necessary to make several preparations of each sample, in order that we may obtain the widest range of possibility for characteristic crystallizations. The following method of procedure will usually give satisfactory results: For a dialyzer use a fairly wide glass tube, over one end of which has been tightly tied a piece of parchment (Fig. 26), or, better, a small dialyzing tube made entirely of parchment. Place about 15 c.c. of saliva in the dialyzing tube, and suspend it in a small beaker or wine-glass which contains an equal volume of distilled water. At the end of twenty-four hours the distilled water will contain the dialyzable salts in nearly the same concentration as existed in the original saliva. Take four previously prepared cell-slides (microscope slides on which a ring of Bell's or other microscopical cement has been placed) and fill each cell full of the dialyzed saliva. Put number *one* in a warm place that it may evaporate rapidly, leave number *two* exposed to the air at the room temperature and it will dry in from half to three-quarters of an hour. Place number *three* under a large beaker, or small bell-jar, and cover number *four* with a cover-glass, and from time to time examine the crystals that

FIG. 26.

PLATE VIII. — ANALYSIS OF SALIVA.
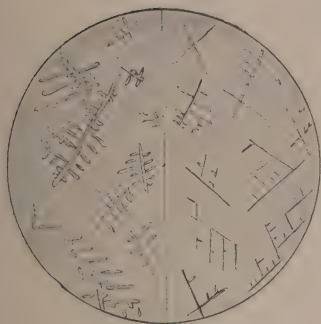
FIG. 1.
Ammonium Chloride.
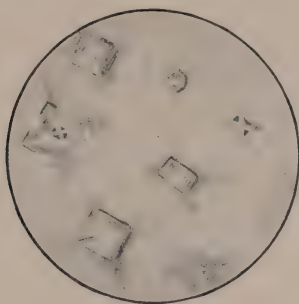
FIG. 2.
Sodium Chloride, $\frac{1}{8}\%$.

FIG. 3.
A, Magnesium Lactate (P. L.).
B, Calcium Lactate (P. L.).

FIG. 4.
A, Magnesium Acid Lactate.
B, Calcium Acid Lactate.
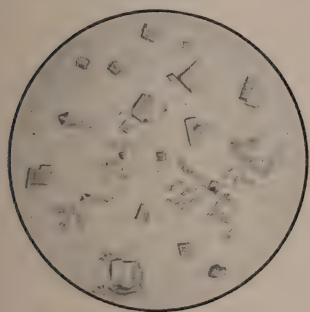
FIG. 5.
Potassium Chloride, $\frac{1}{8}\%$ Solution.
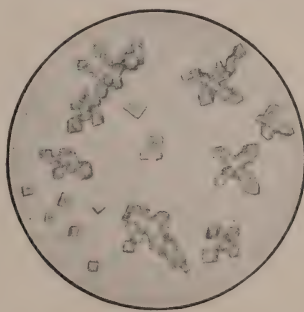
FIG. 6.
Potassium Chloride, $\frac{1}{4}\%$ Solution.

may be formed. Numbers *three* and *four* will probably take several hours, perhaps several days, before crystallization is complete. When the crystals have appeared, the preparation may be preserved by mounting in xylol balsam. In attempting to obtain crystals from the saliva before dialyzation, results are usually unsatisfactory, owing to the presence of mucin and other organic substances which interfere with the crystallization. The crystals obtained by this method are principally sodium oxalate, lactates, and acid lactates of lime and magnesia, and rarely urates of the alkalis. (For forms of these crystals see Plate VIII, Figs. 3 and 4, and Plate II, Fig. 4, pages 316 and 170.)

Tests for Abnormal Constituents.

Acetone, glycogen, and dextrin have already been considered. Urea may be demonstrated as follows: To a given volume of saliva add twice as much alcohol. This serves to precipitate proteins. Filter and evaporate on a water-bath till original volume is reached, or evaporate to less than original volume, and make up with distilled water. Then determine urea by method suggested by Dr. Ferris and given on page 311.

Lactic, *butyric*, and *acetic acids* may each be tested for, qualitatively, by the methods given under gastric digestion (q.v.).

Mercury. — A very delicate test may be made for this metal as follows: Collect as large a sample of saliva as possible, dilute with an equal volume of water, acidify with a few drops of hydrochloric acid, throw in a few very small pieces of copper-turnings, which have been recently cleaned in dilute nitric acid, and boil for at least one-half hour, keeping up the volume by occasional additions of water. Remove the copper-filings, dry thoroughly on filter-paper, and place in a large-sized watch-glass (3 inches). In another watch-glass of similar size place one drop of solution of gold chloride, and quickly invert so that the drop remains hanging on the under side of the glass. Now

place this watch-glass directly over the one containing the copper, so that the chloride of gold shall be suspended directly above the turnings and perhaps a half inch from them, then gently heat the lower watch-glass with a very small flame, when the slightest trace of mercury, which may have been deposited upon the copper, will be volatilized, reducing the chloride of gold, and causing a purplish ring to appear around the edge of the drop. If no reduction of the gold occurs, mercury is absent.

Lead, which occasionally occurs in saliva, may be detected by the methods given under urine.

Microscopical examination of the sediment should be made in every instance. Normal saliva will contain epithelium from various parts of the oral cavity, an occasional leucocyte, and occasional mold fungi, leptothrix, etc. Constituents, which perhaps are not properly classed as normal and at the same time are not pathological, are fat globules, a rare blood-corpuscle, sarcinæ, extraneous material as food particles, starch granules, muscle fibers, etc. An excessive amount of blood, fat, pus, or micro-organisms would, of course, indicate pathogenic conditions. The bacteriological investigation of samples of saliva is always of interest, and may be necessary, but the detailed methods of such investigation do not lie within the scope of this work.

CHAPTER XXXV.

GASTRIC DIGESTION.

DIGESTION begins with the action of the saliva upon the carbohydrates, and if mastication is sufficiently prolonged, the ptyalin may convert an appreciable quantity of starchy food into a more soluble form before it reaches the stomach. In the stomach the amylolitic action of the saliva is stopped by the contact with the gastric juice. A certain amount, however, of salivary digestion takes place within the stomach, due to the fact that considerable time necessarily elapses before the acid of the gastric juice has been secreted in sufficient quantity to completely permeate and acidify the mass of food received from the esophagus. As has been previously shown, a very feeble degree of acidity is conducive to the activity of the amylolytic ferment. The average alkalinity of the saliva, calculated as Na_2CO_3, is about 0.15 of one per cent.

The first step in the gastric digestion is probably the union of the stomach hydrochloric acid with the proteins, forming acid albumins (metaproteins) or allied bodies which are changed by pepsin, which is the active digestive ferment of the stomach, into the proteoses, and slight amounts of the various peptones, following practically the changes produced experimentally on page 418.

Pepsin is an active proteolytic enzyme occurring in the cells of the stomach-wall as pepsinogen; this latter is decomposed by the hydrochloric acid with the formation of free pepsin. Pepsin works only in faintly acid solutions, and in the stomach carries the digestion of proteins but little beyond the stage of the proteoses.

Hydrochloric acid is obtained from the fundus glands by an interchange of radicals between alkaline chlorides and the carbonates of the blood.* The quantity present varies from nothing to 0.3%, the degree of acidity most favorable for peptic activity being about 0.18%.

Aside from HCl, various organic acids may be present in the stomach contents; lactic acid, butyric acid, and acetic acid are the most important of this class, tests for which are referred to under analysis of gastric contents, page 417.

Hydrochloric acid combines with protein substances of the food, forming a rather unstable compound in which condition the acid is known as combined hydrochloric acid in distinction from the free hydrochloric acid which the gastric juice may also contain. The combined acid possesses only in modified form the properties of the free acid, and hence is less liable to stop the digestive action of ptyalin from the saliva.

Rennin is a second enzyme found in the stomach. This, like pepsin, also exists as a zymogen, and is liberated or developed by the presence of acid. Its action is particularly the curdling of milk, i.e., the decomposition of caseinogen (Exp. 253), and consequent coagulation of the casein.

This process involves a splitting of the caseinogen into a slight amount of a peptone-like body and soluble casein. From this latter substance the insoluble curd is produced by the action of the calcium salts contained in the milk. Gastric lipase, or stomach steapsin, a fat-splitting enzyme, is a third enzyme, existing in the stomach in very small quantities, the action of which is comparatively weak and of but slight importance.

It is to be noted that the digestive action of the stomach is only partial, the proteins being split into proteoses and to some extent into peptones, while further action is left for the more active ferments of the pancreatic and intestinal juices.

* Long's Physiological Chemistry.

CHAPTER XXXVI.

PANCREATIC DIGESTION AND BILE.

It may be an aid, in remembering the various digestive ferments, to note that in the saliva we have one principal ferment, ptyalin; in the stomach we have two, pepsin and rennin; in the pancreatic juice, three, trypsin, amylopsin, and steapsin. In addition to these the pancreatic juice contains a ferment similar to rennin known as chymosin.

Trypsin is the proteolytic enzyme of the pancreatic juice. It is a much more energetic digestive agent than pepsin, converting the proteoses into peptones, tyrosin, leucin, and other amino acids. It also differs from pepsin in that it acts in an alkaline medium rather than an acid. Trypsin exists, like other proteolytic enzymes, as a parent enzyme, trypsinogen, which in itself is not a digestive ferment, but which is rendered active (activated) by another substance known as enterokinase.

The enterokinase occurs in the intestinal juice, and seems to be secreted only as it is needed for the activation of the trypsinogen. Enterokinase does not in itself possess digestive power, but its action is destroyed by heat and in this it resembles the enzymes.

Amylopsin, or pancreatic amylase, is the starch-digesting enzyme of the pancreatic juice. Here, again, we have an enzyme much more energetic in its action upon carbohydrates than the ptyalin of the saliva. It converts starch into maltose and to some extent to dextrin. The amylopsin is active in faintly alkaline or very faintly acid solution; more acid, however, retards its action.

The starch-splitting enzyme of the pancreas is dependent

321

upon the presence of electrolytes; if these are removed by dialysis a juice results which is devoid of starch-splitting power. A halogen ion, chlorine or bromine, is apparently essential to the activity of this enzyme.*

Steapsin, lipase, is the fat-splitting enzyme of the pancreatic juice, inactive until it comes in contact with constituents of the bile. It splits the fat, as indicated on page 266, into glycerol and fatty acids, and also acts as an emulsifying agent. The free fatty acids thus formed unite with the alkaline bases found in the intestines to form soaps, which are also active emulsifying agents.

Chymosin, or pancreatic rennin, has practically the same action upon caseinogen as the gastric rennin.

The pancreatic juice and the bile enter the duodenum in very close proximity, and the digestive action of each is dependent, to a considerable extent, upon the presence of the other.

Bile. — A secretion produced by the liver and stored in the gall-bladder, from which it is delivered to the intestines, where it aids materially in emulsification and absorption of the fats.

Composition of Bile. — The composition of bile is very complex as it contains a portion of the waste products of metabolism as well as substances playing an important part in digestion and designed to be reabsorbed into the circulation.

Among the first class are the two principal bile pigments: the bilirubin (bile red) and its oxidation product biliverdin, (bile green). The bile-pigments are derived from the coloring matter of the blood. The appearance of either of these or of their derivatives, in either urine or saliva, is indicative of pathological conditions either of the liver- or bile-ducts, causing obstructions to the outflow of the bile or a destruction of the red-blood corpuscles.† The blood pigments, according to

* Journal of the American Chemical Society, vol. 32, p. 1087, Kendall and Sherman.

† Ogden.

Michaels, are easily demonstrable in the desiccated saliva by means of polarized light.

Cholesterol, ($C_{27}H_{45}OH$?), may also be considered a waste product of the bile. It is excreted with the feces; when retained it is likely to produce " gall stones " which are often found to consist of fairly pure cholesterol with a little coloring matter.

Cholesterol, as its name implies, is an alcohol containing one hydroxyl group and one pair of double-bonded carbon atoms. It is soluble in hot alcohol from which it may be crystallized as thin, colorless plates. (See Plate VII, Fig. 4.)

Two important acids of the bile are taurocholic and glycocholic, existing principally as sodium or potassium salts. Glycocholic acid upon hydrolysis splits into a simpler acid (cholic) and glycocoll, glycocoll being an amino-acetic acid (page 225), which is undoubtedly an antecedent of urea.

Taurocholic acid, on the other hand, splits into cholic acid and taurine, taurine being an amino-ethyl sulphonic acid (page 232).

The Intestinal Juice contains a number of substances playing an important part in the preparation of food material for assimilation. Among them is erepsin (erepase). This is a protein-splitting enzyme acting upon the products of tryptic digestion. It has little power upon the simple proteins, but will split the peptones into amino acids. There are also in the intestinal juice certain amylolytic enzymes, sucrase, lactase, and maltase which continue the digestive action started by amylopsin or by ptyalin of the saliva.

The intestinal juice contains proteolytic enzymes which will hydrolyze the nucleic acids left undigested by other enzymes of the stomach and pancreatic juice. (See Exp. 261 page 421.)

Secretin, excreted by the mucous membrane of the intestine, is a substance differing materially from the digestive ferments in that it is not destroyed by heat. It acts not as an activator

in the sense that it starts specific chemical action, but as an essential constituent for the secretion of the various digestive fluids; i.e., the secretin in the blood starts the flow of pancreatic juice, for instance, which contains the parent enzyme, trypsinogen, which in turn requires the action of enterokinase before it is in condition to perform its work of digestion. Some authorities claim that the secretin itself exists as a pro-secretin, from which it is liberated by action of acid.

DIGESTION IN THE ALIMENTARY CANAL.

Location.	Gland.	Juice.	Ferment.	Acts upon	Changes into	Action.	Second ferment.	Converted into
Mouth	Salivary	Saliva	Ptyalin	Carbohydrates (starch)	{Maltose / Dextrose}	Amylolytic	{Maltase or Glucase}	Glucose
Stomach	Gastric	Gastric	Pepsin	Proteins by HCl into Metaproteins	{Proteoses (albumoses) / Peptones, leucine Tyrosine, etc.}	Proteolytic		
			Rennin	Caseinogen (phosphoprotein)	Casein (Neucleoprotein)	Proteopyknotic[1]		
			Gastric Lipase	Fat	Emulsion	Lipolytic[4]		
Duodenum	Pancreas	Pancreatic	Trypsin	Proteoses	{Proteoses, Peptones, Peptides}	Proteolytic		
			Amylopsin[2]	Carbohydrates (starch)	Maltose, Dextrin	Amylolytic	Maltase	Glucose
			Steapsin[3]	Fats	Emulsion	Lipolytic		
			Pancreatic Rennin	Caseinogen of milk	Casein (proteose-like body)	Proteopyknotic	Lactase	{Glucose / Galactose}
	Liver	Bile	Alkali activators (emulsifying agent)	Fat	Emulsion (glycerol and fatty acid)	Lipolytic		
Intestine	Intestine	Intestinal (Succus Entericus)	Erepsin (erapase)	Tryptic digestion	Amino-acids	Proteolytic		
			Sucrase	Sucrose	{Glucose[8] / Levulose[8]}	Saccharalytic[7]		
			Invertase[5]			"		
			Lactase	Lactose	{Glucose / Galactose}	"		
			Maltase	Maltose	Glucose	"		
			Enterokinase[6]	Trysinogen	Trypsin	Activation		
			Lipase	Fat	Emulsion	Lipolytic		

[1] Protein coagulating or milk curdling enzyme.   [2] Pancreatic amylase.   [3] Pancreatic lipase.   [4] Fat splitting.   [5] Ferment obtainable from intestine and yeast.   [6] Organized ferments.   [7] Sugar splitting.   [8] Invert-sugar.

PART VIII.

URINE.

CHAPTER XXXVII.

PHYSICAL PROPERTIES OF URINE.

URINE is a solution of waste products from the blood. It contains, normally, certain coloring matter, urea, uric acid in combination with alkaline bases, various organic constituents in slight amounts, including, perhaps, albumin and sugar, chloride of sodium, sulphates and phosphates of the alkalis and the alkaline earths. Abnormally the urine may contain albumin, sugar, uric acid as such, bile, salts of the heavy metals, lead, mercury, and arsenic; occasionally albumose, peptones, lactates, acid lactates, oxalates, carbonates, hippuric acid, also organic compounds, resulting from insufficient or imperfect oxidations, as amino acids, leucin, tyrosin, and acetone bodies.

We are to study the urine, not primarily with a view to the diagnosis of renal disease, which is more particularly the province of the physician, but to detect irregularities or deficiencies in the body metabolism, and, as far as possible, we are to study the methods whereby we may correct and regulate the malnutrition which lies at the foundation of many diseases of the oral cavity. As has been previously stated by the author,* if there are diseases of the oral cavity which may have their etiology in some systemic derangement not easily apparent, and if such diseases are to receive the attention of the dentist, he should obtain all possible light on every case, and at present a quantitative analysis of the urine is of greater value than

* International Dental Journal, January, 1905.

any other laboratory aid. In examining a sample of urine to obtain information as above indicated, it is essential that the sample be a portion of the *mixed* twenty-four-hour quantity, and that the total amount of the twenty-four-hour excretion be known. In collecting samples for such analysis a convenient method is to give the patient a one- or two-dram vial, nearly filled with water, and containing three or four drops of a commercial formaldehyde solution, with instructions to empty this into a bottle, or other receptacle, in which the twenty-four-hour sample is collected. Formaldehyde if used in this amount has no effect on the subsequent analysis and is a sufficient preservative.

PHYSICAL PROPERTIES.

Quantity. — The quantity of urine passed in twenty-four hours normally is about 1200 to 1400 c.c. for an adult female and 100 or 200 c.c. more than this for the male. The amount is increased in Bright's disease, in diabetes, and various other pathological conditions, also in cold weather when less moisture is given off from the skin. Normally, the quantity passed during twelve day hours, as 8 A.M. to 8 P.M., will exceed the amount overnight from 8 P.M. to 8 A.M. In cases of chronic interstitial nephritis the twelve-hour night quantity exceeds the day, hence it is desirable in collecting a twenty-four-hour sample to divide the time as suggested, and measure the amounts separately, especially if there is any suspicion of any chronic kidney disease. A diminished quantity of urine may indicate simply a diminished amount of water taken into the system. The urine is diminished pathologically in acute conditions, such as fevers, etc., but such samples rarely reach the dental practitioner.

Color. — The normal color of the urine is usually given as straw color or pale yellow. If lighter than this the color is regarded as pale, if darker than normal it is regarded as high.

The urine may also be colored by various abnormal constituents; it may be bright red from the presence of blood, or chocolate colored with a so-called coffee-ground sediment from decomposed-blood coloring matter. It may be brown to yellow, bright blue or green, due to the ingestion of various drugs. If bile is present in any quantity in the urine it will have a dark or smoky appearance, and, upon shaking, the foam will have a distinctly yellowish or yellowish-green tint.

Appearance. — In addition to the colors mentioned above urine may sometimes have a smoky appearance, due to the presence of hematoporphyrin or iron-free hematin, often found in cases of lead-poisoning. It may have a milky appearance, due to presence of finely divided fat globules, as in chylous urine, due to parasitic disease of the blood. It may be cloudy from four principal causes: first, amorphous urates; second, amorphous phosphates; third, pus; and fourth, bacteria. These may easily be distinguished. The application of a slight degree of heat (insufficient to cause coagulation of albumin) will redissolve the urates, and clear a urine which is cloudy from this cause. A deposit of phosphates is increased by the application of heat, but clears easily upon the addition of a few drops of acetic acid. A urine cloudy from the presence of pus is not cleared by either of these methods, but the cloud settles with comparative rapidity and pus corpuscles are easily recognized by microscopical examination of the sediment. If bacteria are present in sufficient quantity to cause cloudiness, the sample is apt to be alkaline in reaction and will not clear upon filtering. If it is necessary to obtain a clear solution, a little magnesium mixture may be added to the urine, then a little sodium phosphate; warm gently with agitation, when the precipitated ammonium magnesium phosphate will mechanically carry down the bacteria, and a filtrate may be obtained which, after acidifying with dilute acetic acid, will be suitable for an albumin test.

Specific Gravity. — The gravity is most conveniently taken with a urinometer (Fig. 27). Care should be taken in the selection of this instrument so that the scale graduation may be accurate. The fact that the instrument will sink in distilled water at the proper temperature (usually 60° F., $15\frac{1}{2}$° C.) to the zero mark, is not a sufficient proof of its accuracy, as many cheap instruments will do this, and give erroneous readings at the higher markings of the scale. Distilled water is represented by 1000, and the relative increase in the comparative gravity of urines will be easily represented on the scale ranging from 1000 to 1050. As the first two figures of the specific gravity are always the same (10) they are usually omitted from the scale which is made to read from 0 to 50 or 60. The reading should be made, if possible, from underneath the surface of the liquid, as the liquid is usually drawn around the stem by adhesion, so that accurate readings from the surface are difficult. The specific gravity of normal urine is from 1018 to 1022; it decreases in cases where the quantity is much above the normal (polyurias), unless sugar is present. It is increased by the presence of sugar or by concentration, whereby the normal

FIG. 27.

solids are relatively increased. In case the quantity of urine is too small for the determination of the gravity in the usual way, the urinopyknometer, devised and recommended by Dr. Saxe in his " Examination of the Urine," may be employed. See page 307, on specific gravity of saliva.

Reaction. — The reaction of urine is normally acid to litmus-paper, due in part to the presence of acid sodium phosphate, and in part to organic acid combinations, the composition of which is unknown. The degree of acidity is roughly indicated by the intensity of color produced with the carefully prepared litmus-paper. More accurate results may be obtained by a

regular volumetric examination (with N/20 alkali), or by the test for urinary acidities given by Freund and Topfer who suggest the following method:

" To 10 c.c. of the urine add two to four drops of a 1% solution of alizarin. If the resulting color is pure yellow, free acids are present; if deep violet, combined acid salts. If none of these colors appear, there are present acid salts of the type of disodic phosphate. The amount of one-tenth normal hydrochloric acid standard solution required to produce a pure yellow color represents the alkaline salts, while the amount of one-tenth normal sodium hydrate required to cause a deep violet represents the acid salts."

CHAPTER XXXVIII.

NORMAL CONSTITUENTS OF URINE.

THE more important normal constituents of the urine are urea, uric acid (combined as urates), chlorides, phosphates, sulphates, indoxyl, coloring matters; traces of mucin, organic acids, carbonates, hippuric acid, creatin, and creatinin may also be present. The total normal solids are composed approximately of 50% urea, 25% chloride of sodium; at least one-half of the remainder are phosphates and sulphates. We see that the constituent which most influences the specific gravity is the urea, and in normal samples the specific gravity is an index of the amount of urea present. The total solids may be calculated by multiplying the last two figures of the specific gravity by $2\frac{1}{3}$,* which will give approximately the number of grams of solids in one liter of urine; from this the solids in the twenty-four-hour amount may be easily calculated.

UREA.

The chemistry of urea has been already considered (page 237).

Detection. — A qualitative test for this substance is obviously superfluous, although such may be made by obtaining the crystals of urea nitrate or oxalate (page 238). The quantity of urea is of great importance, especially in cases where there is any question in regard to the body metabolism or the amount of nitrogen excreted. By far the greater proportion of all nitrogenous waste is eliminated by the kidneys in the form of urea, a comparatively slight amount as other nitroge-

* Coefficient of Hæser.

nous constituents of the urine, a still smaller amount in the feces, and traces only by other avenues. The urea may be quantitatively determined by various methods, the hypobromite method being the most practical. See reaction on page 238.

Quantitative Determination. — There are various forms of apparatus used in connection with this process.

The one devised by Dr. Squibb is pictured in Fig. 28. It has been quite generally used; hence its description is given. It is not recommended, because a source of considerable error
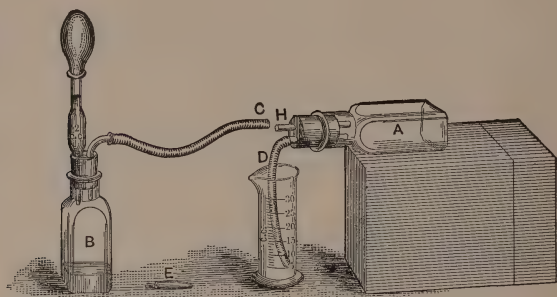
Fig. 28.

lies in the fact that the gases (CO_2 and N) evolved from the urea are very apt to be driven over into bottle *A before all* the CO_2 has been absorbed by the reagent in *B* and consequently the results are higher than they should be.

The first step in the use of this apparatus is to completely fill the bottle *A*, including the tubes *D* and *H*, with water, with the glass plug *E* closing the lower end of *D*. Next put 5 c.c. each of a 40% solution of caustic soda and a bromine solution in potassium bromide * into *B*. Place the stopper in *B* and connect the tube *C* at *H*, then fill accurately the 2-c.c. pipette with urine. Place in position in the stopper of *B* as shown in the cut, remove *E* from the rubber tube *D*, and allow

* For preparation of this solution see Appendix.

D to fall to the *bottom* of the graduate as indicated. Pressure is now applied to the bulb of the pipette, so that the 2 c.c. of urine is forced with moderate rapidity into the bottle. As the pressure on the bulb is released, water will be drawn back into *A*, and it is essential that the end of *D* be under water during this part of the process. Bottle *B* should be agitated to insure complete decomposition of the urea. Nitrogen and carbon dioxide are at once evolved according to the reaction on page 238. The 40% solution of caustic soda is strong enough to absorb and hold the CO_2. The nitrogen passes into *A*, forcing a corresponding volume of water into the graduate. This volume of gas, read in cubic centimeters of the water, will give the percentage of urea in the sample examined, 1 c.c. of nitrogen being equivalent to 0.126 gram of urea.

FIG. 29.

The Doremus-Hinds apparatus shown in Fig. 29 gives a perfectly satisfactory method for the estimation of urea by the hypobromite method. The reagent, equal parts of bromine solution and 40% NaOH (Appendix, page 427), is introduced into *R* and the tube completely filled. The tube *U* is next filled exactly to the zero mark, then by means of the stop-cock *S* 1 c.c. of urine is allowed to enter *T* a few drops at a time and slowly enough to prevent any escape of gas through *R*. The gas rises in small bubbles through a comparatively long tube and remains in contact with the reagent which insures perfect absorption of CO_2, thus overcoming the greatest objection to the Squibb's apparatus.

The tube *T* is graduated to read centigrams of urea in 1 c.c. of urine.

A more accurate determination of urea depends upon the conversion of urea into ammonia by various methods which make quantitative application of the Kjeldahl determination
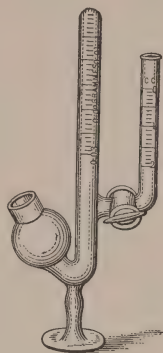
of nitrogen.   These are given in excellent detail in Hawk's Fifth Edition of " Practical Physiological Chemistry " and to this work the student is referred.

URIC ACID.

Uric acid and its antecedents, the xanthin bases, are derived from the decomposition of nuclein and nucleoprotein.   For chemistry of this substance, see pages 240 to 243.   The uric acid is increased by a highly nitrogenous diet and certain vegetable substances which contain purin (page 241) derivatives, such as coffee, tea, and cocoa.   The so-called red meats, beef, mutton, etc., are regarded as the most abundant source of uric acid and urates.   As previously suggested uric acid does not occur in normal urine as such, but is combined with the alkaline bases.

Determination. — It is unnecessary to make a qualitative test in urine, as urates are always present.   If a qualitative test is desired the murexide test, as given on page 394, is available. Uric acid and allied constituents of the urine are conveniently determined quantitatively by the centrifugal method as devised by Dr. R. Harvey Cook.*   The detail of this method is as follows: Measure 10 c.c. of urine into a graduated tube, used in the centrifugal machine, add a few grains of sodium carbonate, and about 3 c.c. of strong ammonium hydrate. Place in the centrifuge, and allow to run for one or two minutes, then carefully decant the clear urine into another graduate tube, leaving the precipitate which consists of earthy phosphates.   The bulk of this precipitate may be noticed and an idea obtained as to whether the earthy phosphates are present in normal quantities or not.   To the clear urine add 2 or 3 c.c. of ammoniacal silver-nitrate solution ($AgNO_3$, 5 grams; distilled water, 80 c.c.; strong ammonia, 20 c.c.), and run in the centrifuge till the precipitate of silver urate has reached its

* Medical Record, Mar. 12, 1898, page 373.

lowest obtainable reading. The ammonia will prevent the precipitation of chlorides and, unless iodides or bromides are present, the precipitate will be fairly pure silver urate, each tenth of a cubic centimeter of the precipitate being equivalent to 0.001176 gram of uric acid in the 10 c.c. of urine used, or 0.01176%.

The silver precipitate is by no means pure silver urate, many of the other nitrogenous bases in urine forming insoluble silver salts. These occur only in very slight traces; so, for clinical purposes, the method is available unless the sample contains bromides or iodides, when iodide or bromide of silver will be formed, insoluble in the amount of ammonia usually used. More accurate results may be obtained by either Hopkins' or Folin's method. These are somewhat similar and consist of precipitation of the uric acid as ammonium urate. 100 to 200 c.c. of urine is used and the precipitation effected by a saturated solution of NH_4Cl (Hopkins' method) or ten grams ammonium sulphate (Folin's method).

The precipitate is washed in the reagent and dissolved in boiling water and the amount of uric acid determined by titration with N/20 permanganate of potassium. Each cubic centimeter of $KMnO_4$ used is equal to 0.00375 gram of uric acid.

Ammonia Determination.

The amount of ammonia normally present in urine is about 0.7 gram in the 24-hour amount. Ammonia is increased in any systemic condition resulting in an increase of acidic elements (Acidosis), or upon ingestion of ammonium salts of inorganic acids, i.e., salts not easily oxidized to urea.

Normally, the quantity of NH_3 follows more or less closely the urea and the protein metabolism, and amounts to about one-twentieth of one per cent. (0.05%) or about 0.7 gram in twenty-four hours.

Determination may be made as follows:

Folin's New Method. — Measure, by use of standardized

" Ostwald pipette," 1 or 2 c.c. of urine into a large Jena test-tube. Then proceed exactly according to method given for saliva on page 310.

Formaldehyde Method. — Place 10 c.c. urine in a 250 c.c. Erlenmeyer flask, add 50 or 60 c.c. H_2O, titrate with N/10 NaOH with phenolphthalein as an indicator. The amount of NaOH used will represent total acidity of sample.

After exact neutralization add 10 c.c. of previously neutralized commercial formaldehyde solution and titrate *again* with N/10 NaOH. The *second* amount of alkali added represents ammonia as follows:

$$4 NH_4Cl + 6 CH_2O + 4 NaOH = N_4(CH_2)_6 + 10 H_2O + 4 NaCl.$$
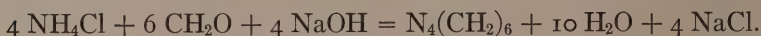
As the ammonium salts and the caustic soda react molecule for molecule it is possible to make calculation for quantity of NH_3 by multiplying the N/10 factor (0.0017) by the number of cubic centimeters of N/10 NaOH used.

In cases of diabetes when the ammonia reaches a comparatively large amount the figures obtained by this process will be found to be a little high, as amino acids are also acted upon by the NaOH, and will be calculated as ammonia, but for ordinary work of clinical comparisons this method is very simple and sufficiently accurate.

This method is not affected by urea, uric acid, creatin, creatinin, purin bases, or hippuric acid.*

CHLORIDES.

The chlorides are represented in the urine chiefly by sodium chloride. This is present to the extent of from twelve to twenty grams in twenty-four hours. An increase above this quantity

---

* Dr. Hans Malfatti in Zeit. für Anal. Chemie, 47, page 273.

Note. — See also the Vacuum Distillation Method, giving very exact results when properly carried out:

H. Björn Andersen und Marius Lauritzen, Zeit. für Physiol. Chemie, 64, page 21.

is unusual, although it simply indicates an increase in the ingested salt, and is without clinical significance. The chlorine is diminished in dropsy, acute stages of pneumonia, and in fevers generally.

Detection. — The usual qualitative test with silver nitrate and nitric acid is employed for detection of chlorine in the urine. If one drop of a strong solution of silver nitrate (1 to 8) is allowed to fall into the wine-glass in which the albumin test has been made (q.v.), the appearance of the resulting precipitate will give a rough idea of the quantity of chlorine present. If a solid ball of silver chloride is formed which does not become diffused upon gently agitating the contents of the glass, the chlorine is normal or increased. If the precipitate falls as a cloud distributed throughout the liquid, the chlorine is diminished. The chlorine may be determined by precipitation with silver nitrate in 10 c.c. of urine, and the precipitate settled in a centrifuge-tube to constant reading, but this method is not recommended, as the precipitate is a bulky one, and usually takes a long time for thorough settling. The titration with silver nitrate, using potassium chromate as an indicator, really takes less time, and is much more accurate. This titration is made in the usual way (see page 159), except that, inasmuch as phosphates and urates are also precipitated, from three-tenths to 1 c.c. may be deducted from the amount of the silver-nitrate solution used according as it is much or little, thus allowing for these substances. An accurate titration of chlorine is described on page 161. But, as a rule, the simpler method gives results which for clinical purposes are equally valuable with those of this more tedious though more accurate process.

PHOSPHATES.

The phosphates in the urine are of two kinds, the alkaline phosphates, Na_2HPO_4 and NaH_2PO_4, etc., and the earthy phosphates represented by the magnesium and the calcium phos-

phates. The phosphates are normally present to the extent of two and a half to three and a half grams, calculated as P_2O_5 (in twenty-four hours).

The triple phosphates, ammonium magnesium phosphates (Plate IV, Fig. 2, page 172), are the forms in which phosphoric acid is usually found in urinary sediment. Crystals of acid calcium phosphate are occasionally found, and resemble the acid sodium urate in form (Plate X, Fig. 3, page 355), except that they are usually a little broader and more often occur in fan-shaped clusters. They may be distinguished by treatment with acetic acid, which dissolves the calcium phosphate promptly, while the urate is slowly dissolved and crystals of uric acid appear after a little time. The phosphates are deposited from neutral or alkaline urines and when this precipitation takes place within the body, the crystals cause more or less irritation to the urinary tract and may form aggregations which result in calculi. Phosphates are supplied by either a cereal or meat diet. They may be much increased in diseases accompanied by nervous waste, or by softening and absorption of bone. Phosphates are diminished in gout, in chronic diseases of the kidney, and during pregnancy.

Detection. — A qualitative test for earthy phosphates (E.P.) may be made by taking a test-tube half full of urine, and making alkaline with ammonium hydrate. When the precipitate has thoroughly settled, if it is about 1/4 to 1/2 inch in depth, it represents normal, earthy phosphates. If this mixture is now filtered, the alkaline phosphates (A.P.) may be determined in the filtrate by the addition to the solution of one-third its volume of magnesium mixture.* The precipitate after settling will be 1/2 to 3/4 of an inch in depth if normal. The total phosphates may be determined in the centrifugal machine by adding 5 c.c. of magnesium mixture to 10 c.c. of urine. Each tenth of a cubic centimeter of the centrifugalized

* See Appendix.

sediment will be equivalent to 0.00225 gram of P_2O_5 in the 10 c.c. used.

A more accurate determination of the total phosphoric acid may be made by the titration with uranium nitrate or acetate solution as follows:

Reagents Required. — *First.* A standard uranium solution may be prepared as follows: Dissolve 35.5 grams of pure uranium nitrate or acetate in about 800 c.c. of distilled water; add three or four c.c. of glacial acetic acid and heat it enough to complete solution. Allow to stand over night, filter carefully, and make up to 1000 c.c. Standardize this solution against crystallized microcosmic salt by dissolving 14.721 grams of the pure salt ($NaNH HPO_4 . 4 H_2O$) in sufficient water to make 1000 c.c. Then titrate 20 c.c. of this solution, to which has been added 30 c.c. of water and 5 c.c. of sodium acetate solution, with the uranium solution (method of titration is given under process below).

The uranium solution should then be adjusted (diluted) so that it will take exactly 20 c.c. for this titration, when one c.c. of the uranium will be equivalent to five milligrams of P_2O_5.

Second. A sodium acetate solution containing 100 c.c. of 30% acetic acid and 100 grams of sodium acetate in enough distilled water to make 1000 c.c.

Third. An indicator consisting of a saturated solution of potassium ferrocyanide.

Process. — Place 50 c.c. of urine with 5 c.c. of sodium acetate solution above described in a small Erlenmeyer flask and heat nearly to the boiling-point. Titrate, while hot (80° or above), with the standard uranium solution till a drop of the mixture placed on a white porcelain tile with a drop of the indicator (K_4FeCy_6) gives a distinct brown color. This method of determining the end point is known as " spotting " and with a little practice gives very accurate results.

The number of cubic centimeters of uranium solution multi-

plied by 0.01 will give the weight of P_2O_5 in 100 c.c. of urine
(1 c.c. of reagent being equal to 0.005 gram P_2O_5).

This same process may be used for saliva by diluting the
reagent one part to five, and preparing the sample for titration
as follows: Take from 2 to 5 c.c. saliva, add sufficient alcohol
to make 10 c.c. of mixture, warm, and filter. This serves to
separate the protein substance. Take 5 c.c. of the filtered
solution and titrate with the diluted uranium solution as by
the process given above for urine. In this case, of course, 1 c.c.
of the standard uranium will represent one milligram of P_2O_5
rather than five.

Sulphates.

The sulphates in the urine are present as alkaline sulphates,
K_2SO_4 and Na_2SO_4; also as ethereal sulphates, represented by
such compounds as indoxyl potassium sulphate, page 253.

Detection and Determination. — The sulphates may be de-
tected by precipitation with barium chloride in hydrochloric
acid solution. If the precipitate is obtained from 10 c.c. of
urine and centrifugalized to constant reading, the per cent. of
sulphuric acid by weight will be one-fourth of the volume per
cent. of the precipitate. The sulphates follow rather closely
the urea, and their determination is not of great importance.
They are increased in acute fevers, diminished in chronic diseases
generally, and markedly diminished in carbolic-acid poisoning.
(Ogden.)

Determination of Total Sulphur. — (J. Benedict, Biol. Chem.,
6, 363; W. Denis, J. Biol. Chem., 8, 401.) To 25 c.c. of urine
contained in a porcelain evaporating dish (10–12 cm. diameter)
add exactly 5 c.c. of a solution containing 25 per cent. copper
nitrate, 25 per cent. sodium chloride, and 10 per cent. ammonium
nitrate. Evaporate to dryness over a water-bath. Then heat
over a flame, gradually increasing the heat until the dish is
red hot, and continue heating for 10 to 15 minutes. Allow to

cool. Add 20 c.c. dilute hydrochloric acid and warm gently. Rinse into a flask or beaker by means of about 100 c.c. hot water. Heat to boiling, and add drop by drop 25 c.c. of a 10 per cent. barium chloride solution. Filter, wash, ignite, and weigh.

Coloring Matter. — Urobilin, an important coloring matter of the urine, exists as a parent substance or chromogen to which has been given the name urobilinogen. This undergoes decomposition by action of light with liberation of urobilin.

Urobilin is without doubt derived from the bilerubin of the bile, which, in turn, comes from the hemochromogen of the blood. Dr. J. B. Ogden is authority for the statement that "it is safe to infer that the amount of urobilin in the urine is a measure of the destruction of the hemoglobin or blood pigment."

Urochrome is a pigment to which the yellow color of urine is chiefly due. Uroerythrin and urorosein are less important, existing only in very slight quantities, but they are responsible for colors of some sediments and of decomposition products which are noticed in analysis.

Soluble Salts.

An examination of the soluble salts of the urine is easily and often profitably made by simply allowing a large drop to evaporate spontaneously and examining the residue with the micropolariscope. The alkaline chlorides are often seen but they do not polarize light. Crystalline phosphates, sulphates, urates, and oxalates do polarize light and may frequently be detected by their characteristic forms. The value of determination of soluble oxalates in this way is suggested on page 356.

Indoxyl.

The indoxyl is of considerable importance, as an increase above the normal amount is indicative of increased putrefaction of nitrogenous substances (tryptophan) taking place in the

small intestine. Indoxyl may also be increased by acute inflammatory process of the peritoneal cavity. Ordinary constipation does not increase the indoxyl. The test for indoxyl depends upon the oxidation of the indoxyl potassium sulphate to indigo blue according to the following reaction:

$$2\ C_8H_6NKSO_4 + O_2 = 2\ C_8H_5NO + 2\ KHSO_4.$$
Indoxyl potassium sulphate.   Indigo.
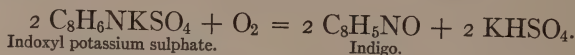
Note. — As tryptophan is a necessary constituent of any nitrogenous substance from which indoxyl is produced, it may happen that a few protein substances, such as gelatin which does not contain tryptophan, might be used in undue proportion and an excessive putrefaction would not be accompanied by indoxyl, but the nitrogenous food substances generally contain sufficient tryptophan to make the first statement of this paragraph practically true.

Detection and Determination. — 15 c.c. of strong HCl is placed in a wine-glass, and a single drop of concentrated nitric acid added; then thirty drops of urine are stirred into the mixture. If indoxyl is present, an amethyst color develops in from five to fifteen minutes. If the color is purple, the indoxyl is increased. Variation of the amount of indoxyl within normal limits is rather wide, and the indoxyl may be reported as high or low normal, increased, or diminished.

CHAPTER XXXIX.

ABNORMAL CONSTITUENTS OF URINE.

THE principal abnormal constituents are albumin, sugar, acetone, bile, and various crystalline salts, discoverable either by microscopical examination of the sediment, or by evaporation of a clear fluid, and examination with the micropolariscope.

Metallic substances, arsenic, lead, and mercury are occasionally present, and tests should be made for them when general symptoms or the conditions of the kidney indicate metallic poison. ALBUMIN is probably present in minute traces in the majority of urines. When in sufficient quantity to be detected by the usual laboratory methods, it is essential that we learn the source from which it has been derived, for the simple presence of even a considerable trace of albumin may be of but slight clinical importance. Albumin may indicate either a pathological condition of the kidney, which allows the entrance into the renal tubules of serum-albumin from the blood, or it may indicate a change in the composition of the blood, whereby the albumin passes more easily through the renal membranes, or its presence may be due to irritations from various sources of the urinary tract; and, as regards the bearing of albuminurias on dental disease, it is sufficient simply to determine whether renal disturbance is primary or secondary to some other trouble, such as heart disease; or purely local, as when caused by irritation due to crystalline elements.

Detection. — Albumin may be detected by either of two simple methods. It is often desirable to use both of these methods, thereby eliminating possible confusion from the

presence of substances other than albumin, which may respond to one of the two tests, but not to both.

The first consists simply in underlaying about 25 c.c. of *filtered* urine in a wine-glass with concentrated nitric acid. The wine-glass should be tipped as far as possible and the acid allowed to run very slowly down the side. This method is preferable to the use of the apparatus known as the albumino-scope or Horismascope (Fig. 30). As this latter method does

FIG. 30.
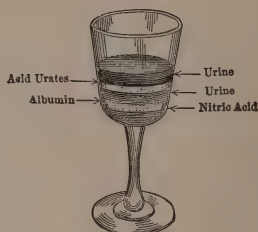
FIG. 31.

not provide for sufficient mixing of nitric acid with the sample, the albumin is shown by a narrow white ring *at* the plane of contact of the two liquids. A white ring *above* the plane of contact is not albumin, but is composed of acid urates, indicating an excess of urates in the sample (Fig. 31). The albumin, in distinction from this band, occurs directly above the acid and is usually reported as the slightest possible trace when just discernible; as a slight trace, when well marked, but not dense enough to be seen by looking through the liquid from above; as a trace, when the white cloud may be seen by looking down into the glass from above and a large trace if plainly visible in this way.

Acetic acid and heat method of testing for albumin is the other method referred to in the preceding paragraph. It is of about the same delicacy as the nitric acid test, and is less liable to respond to substances other than albumin. It is made as follows:

A test-tube is filled two-thirds full of perfectly clear filtered urine, one drop of acetic acid added and the upper half of the sample boiled. The tube can easily be held in the hand by the lower end. After boiling, if the tube is examined before a black background, a slight cloudiness or turbidity resulting from coagulated albumin can be easily detected in the upper part of tube. Anything more than a trace should be determined in the centrifugal machine by mixing 10 c.c. of filtered urine with about 2 c.c. of acetic acid and 3 c.c. of potassium ferrocyanide solution. Each tenth of a cubic centimeter of the precipitated albumin, when settled to constant reading, indicates one-sixtieth of one per cent. albumin by weight. This factor is fairly correct up to four- or five-tenths of a cubic centimeter of precipitate; beyond this it is of little value, and the albumin is best determined quantitatively by measuring 50 or 100 c.c. of urine into a small beaker, adding a drop of acetic acid, and boiling, which will completely precipitate the albumin. It may then be filtered into a counterpoised filter, thoroughly washed, first in water, next in alcohol, and lastly in ether, dried at a temperature a little below the boiling-point of water, and weighed. Esbach's method may be of value in some instances, and is carried out as follows:

FIG. 32.

Fill the albuminometer (Fig. 32) with urine to the line *U*, and then add the reagent * to the line *R*; close the tube, mix the contents thoroughly, and allow to stand in an upright position for twenty-four hours. At the end of that time the depth of precipitate may be read by the figures on the lower part of the tube, these figures representing tenths of one per cent. of albumin, or grams of albumin in a liter of urine. If a sample of urine contains more albumin than is easily estimated

* Esbach's reagent consists of picric acid, 10 grams; citric acid, 20 grams, and distilled water sufficient to make one liter.

by the centrifugal or Esbach's method, approximate results will be obtained by diluting with several volumes of distilled water, until the quantity of albumin precipitated is within the limit of the test. The proteoses occasionally occur in the urine, and are distinguished from albumin by the fact that they redissolve at a boiling temperature. If filtered while hot, albumin, which usually accompanies them, will remain on the paper, while albumose will separate from the clear filtrate as it cools.

SUGAR.

Sugar in urine represents a perverted process of oxidation for which the pancreas is largely responsible. The liver also often plays an important part in cases of diabetes, but just how this is done is not clearly known. Sugar in the urine does not of necessity indicate diabetes any more than albumin indicates Bright's disease. Many cases of glycosuria are of a temporary nature and respond readily to dietary treatment. Whenever sugar is found it is-desirable to make tests upon both a fasting and an after-meal sample, such as might be obtained before breakfast and one hour after dinner. If the fasting sample is comparatively free from sugar, it indicates that the glycosuria is of a temporary nature and due to faulty metabolism, rather than to any organic disease of the liver or pancreas.

Detection. — Sugar in the urine may be detected by several general carbohydrate tests, as previously given.

Fehling's test. This test is very generally employed (Exp. 167, page 401). It is best, however, to modify it by bringing the Fehling's solution to active ebullition, adding from five to thirty drops of the suspected sample and allowing to stand without further heating. This prevents possible reduction of the sugar by xanthin bases or other occasional constituents of the urine, which might give misleading results if the mixture were boiled after addition of the sample. There is less danger of trouble of this sort if the gravity of the urine is below normal.

If it is necessary to make a rapid test, the mixture may be boiled after the urine is added, and in case the result is negative there is no need of further test; if, however, a slight reduction of the copper solution takes place, it will be necessary to repeat the test, using the precaution above given. Quantitatively, sugar may be determined by the use of Fehling's solution as follows:

If the urine contains more than a trace of albumin, this substance should be removed by adding a drop of acetic acid and heating; after filtration the sample should be cooled and restored to original volume with distilled water. If specific gravity of the urine is more than 1025, it should be diluted to ten times its volume with distilled water (urine, one part; water, nine). If the gravity is less than 1025, dilute it to five times its volume, mix, and fill a 25 c.c. burette. In a 250 c.c. flask place 10 c.c. each of the alkaline tartrate and copper sulphate solutions (Fehling's solution), and add about 100 c.c. of distilled water. Place the flask over a Bunsen burner, and bring to a boil. If no change takes place after a minute or two of boiling, add the solution from the burette gradually, until the precipitate becomes sufficiently dense to obscure the blue color of the solution. Continue to boil for one or two minutes, then remove from the flame and watch carefully the line directly beneath the surface of the liquid, which will appear blue until all of the copper has been reduced to the red suboxide. The solution should be kept at the boiling-point throughout the entire operation, except in making the examination of the meniscus between the additions of the diluted urine. These additions must be made very carefully, and as the process nears completion not more than one or two drops should be added at a time. When the blue color has entirely disappeared, and the line of meniscus has become colorless, note the number of cubic centimeters of dilute urine used, and calculate that in that quantity there is an equivalent of 0.05 gram of glucose;

in other words, 0.05 gram of glucose will exactly reduce the amount of Fehling's solution used, and from this fact the amount of glucose in the entire twenty-four hour amount of urine is easily calculated. If the titration is carried beyond the proper "end point" the meniscus will appear yellow instead of colorless.

Benedict's test. The following application of Benedict's solution to the detection of sugar in urine is taken from a paper by Stanley R. Benedict in the Journal of the American Medical Association, October 7, 1911. "For the detection of glucose in urine about 5 c.c. of the reagent are placed in a test-tube and *eight to ten drops* (*not more*) of the urine to be examined are added. The mixture is then heated to vigorous boiling, kept at this temperature for one or two minutes, and allowed to cool spontaneously. In the presence of glucose the *entire body of the solution will be filled with a precipitate*, which may be red, yellow or greenish in tinge. If the quantity of glucose be low (under 0.3 per cent) the precipitate forms only on cooling. If no sugar be present the solution either remains perfectly clear, or shows a faint turbidity that is blue in color, and consists of precipitated urates. The chief points to be remembered in the use of the reagent are (1) the addition of a small quantity of urine (8 to 10 drops) to 5 c.c. of the reagent, this being desirable not because larger amounts of normal urine would cause reduction of the reagent, but because more delicate results are obtained by this procedure, (2) vigorous boiling of the solution after addition of the urine, and then allowing the mixture to cool spontaneously, and (3) if sugar be present, the solution (either before or after cooling) *will be filled from top to bottom with a precipitate*, so that the mixture becomes opaque. Since bulk, and not color, of the precipitate is made the basis of a positive reaction, the test may be carried out as readily in artificial light as in daylight, even when examining for very small quantities of sugar."

The fermentation test (Exp. 172, page 401) may also be used to detect the presence of sugar and, approximately, the amount.

The fermentation test for sugar is a convenient and easily made qualitative test, it being only necessary to fill a fermentation tube (Fig. 38, page 401) absolutely full of urine to which a small portion of yeast has been added, and to allow the tube to stand in a warm place for several hours. Any collection of gas in the top of the tube will indicate the presence of sugar. This method may also be used as a quantitative test for sugar by taking two portions of the same sample, adding yeast to one, and using the other as a control. At the end of twenty-four hours, CO_2 is removed from fermented sample, the specific gravity of both samples is carefully taken, and the loss of density in the fermented sample is calculated as sugar by multiplying the number of degrees lost in gravity by 0.23, water being considered as 1000.

The phenyl-hydrazine test may be used as a confirmatory test or in cases where very minute quantities are suspected. This test is considered about ten times as delicate as the Fehling's test; consequently, it may show small amounts of sugar which are not detected by the more rapid process.

The optical analysis for sugar may be made with a polariscope, preferably constructed for use on urine. This determination depends upon the ability of glucose to rotate the plane of polarized light towards the right, the degree of rotation indicating the amount of sugar in a pure solution. Of course, allowance or correction must always be made for the presence of any substances which will rotate the light in the opposite direction, such as albumin, levulose and β-oxybutyric acid.

For the detail of construction and use of the polariscope, the student is referred to the more complete works on urine analysis by Ogden, Holland, or Purdy.

ACETONE.

Acetone may occur in the urine as a result of various pathological conditions and according to von Noorden they are all due to some one-sided perversion of nutrition. The acetonurias attendant on diabetes, scarlet fever, pneumonia, small-pox, etc., are of less practical interest to the dental practitioner than those more often overlooked by the medical profession, and which indicate improper diet, possibly resulting in serious malnutrition. The following points may be noted: In advanced stages of diabetes, acetone appears in the urine accompanied by diacetic acid. An increased ingestion of proteins may result in the appearance of acetone, in which case the direct cause is more an " insufficient utilization of carbohydrates " * than the increase of protein. Acetone may result from the oxidation of β-oxybutyric acid. Diacetic acid is first formed, and subsequently the carboxyl group is replaced by an atom of hydrogen, as shown by the following graphic formulæ:

$$\beta\text{-oxybutyric acid: } CH_3 - CHOH - CH_2 - COOH.$$
$$\text{Diacetic acid: } CH_3 - CO - CH_2 - COOH.$$
$$\text{Acetone: } CH_3 - CO - CH_3.$$

Detection. Acetone may be detected in the urine by the production of iodoform, as described under analysis of saliva on page 313, but it is not in this case nearly so delicate a test on account of the odor and acid character of the urine. A more useful test is known as Legal's test and is made as follows: To a third of a test-tubeful of urine add a few drops of a freshly prepared and fairly concentrated solution of sodium nitroprusside, next add two or three drops of strong acetic acid, and then a considerable excess of ammonia. If the contents of the tube are mixed by a rather rapid rotary motion without inverting or violent shaking, the ammonia will not reach the bottom

* von Noorden's Diseases of Metabolism and Nutrition.

of the tube, and the presence of acetone will be indicated by a violet-red band above the layer of acid liquid. If much acetone is present a deep violet to purple color is obtained.

Diacetic Acid occasionally occurs in urine as an abnormal constituent most commonly in advanced stages of diabetes, usually accompanied by acetone and β-oxybutyric acid. It may be detected by adding to the urine a little ferric chloride, when a dark wine-red color is produced. If a precipitate of ferric phosphate is obtained, filter the urine and examine the filtrate for color. This test may be made fairly distinctive for diacetic acid by boiling and cooling a second portion of the urine previous to making the test, when the result will be negative if the color at first produced was due to diacetic acid.

β-oxybutyric Acid. — This substance usually accompanies diacetic acid as above stated. Determinations of the quantity present cannot be made by any simple method. Perhaps the most practical method is by Bloor's nephelometer, page 296.

BILE.

Bile may occur in the urine as such, due to pathologic conditions of the liver- or bile-ducts, as stated on page 322. The coloring matters of the bile may also occur from causes aside from lesions of the liver. A urine containing bile or bile-pigments is always more or less highly colored, and upon shaking the foam will be of a yellow or greenish-yellow color. Albumin and high indoxyl accompany the presence of bile and there is also usually considerable renal disturbance. It may be detected by carefully adding to one-half a wine-glass of the suspected sample a few cubic centimeters of the alcoholic solution of iodine (tincture of iodine). A green color will be observed just beneath the line of contact of the two liquids (page 423). The test may be conveniently made by placing the iodine first in the wine-glass and then with a pipette introducing the urine beneath the iodine solution.

METALLIC SUBSTANCES.

Arsenic, mercury, and lead are the three metals which it may be necessary to look for in a sample of urine. The method for the detection of mercury, given on page 317, is applicable for this purpose.

Arsenic may be detected by the Marsh-Berzelius test (page 36), after oxidizing all organic matter. The process may be carried out as follows: Evaporate to dryness a liter of urine, to which 200 c.c. of strong nitric acid has been added; add to the residue, while still hot, from 15 to 20 c.c. of concentrated sulphuric acid. This must be done in a large porcelain evaporating-dish, or else the acid must be added very slowly to prevent frothing over and loss of a portion of the sample. After the action has quieted down the whole mixture may be transferred to a 500 c.c. Kjeldahl flask and heat applied, gradually at first, and then more strongly. It will be necessary to add from time to time small portions of nitric acid and possibly a little more sulphuric acid; as the oxidation progresses the liquid in the flask becomes lighter in color and at the completion of the process is water-white, even when the temperature is increased so that sulphuric-acid fumes are given off. After cooling, the strongly acid liquid is diluted with four or five times its volume of water, filtered, if necessary, to remove excessive amounts of earthy sulphates, and is then ready for the arsenic test.

Lead. — The sample of urine to be tested for lead should measure at least 1000 c.c., and should be tested for iodine to insure the fact that the patient has been under treatment with potassium iodide to dissolve lead salts, otherwise a negative result may be obtained when lead is actually present and poisoning the system. Oxidize the sample in precisely the same manner as when making the arsenic test, up to the point of diluting the strong acid solution with water; then, in this case,

PLATE IX. — URINE.
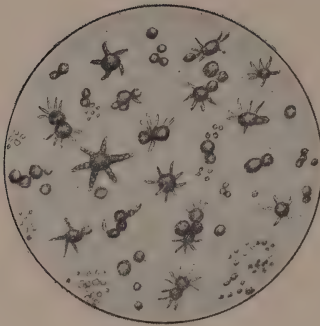
FIG. 1.
Ammonium Acid Urate.

FIG. 2.
Spermatozoa.
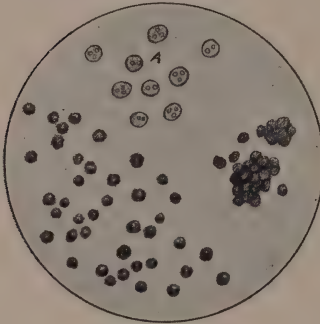
FIG. 3. — Pus.
A, After addition of Acetic Acid.

FIG. 4.
Renal Casts.
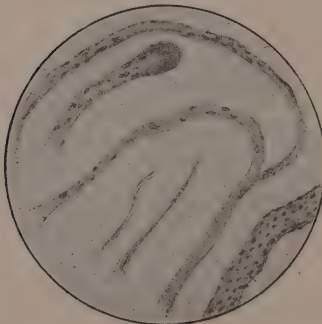
FIG. 5.
False Casts and Mucin.
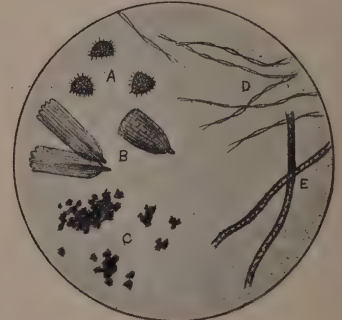
FIG. 6.
A, Lycopodium; *B*, Moth-scales; *C*, Cork;
D, Cotton-fibres; *E*, Wool-fibres.

use rather less water for the dilution, allow to cool, and neutralize with Squibb's ammonia, acidify quite strongly with acetic acid, and pass H_2S gas into the solution. It is desirable to leave the solution saturated with H_2S for at least twelve hours. Then filter, and without washing dissolve the precipitate in warm dilute nitric acid, evaporate the HNO_3 solution to dryness, add 5 c.c. of water, make alkaline with a drop or two of ammonia, and again acidify with acetic acid and add a solution of bichromate of potash.* Allow to stand several hours, filter off the chromate of lead, wash several times with distilled water, and lastly with H_2S water when the lead chromate will blacken from the formation of lead sulphide. This stain is a superficial one and disappears upon standing, but when the process is conducted in this way it constitutes a very delicate and satisfactory test for lead in either urine or saliva.

Urinary Sediments.

The sediment which settles from a sample of urine upon standing consists normally of a slight amount of mucin and epithelial cells. It may contain also bacteria and a considerable variety of extraneous matter, including starch grains, various vegetables spores, yeast cells, fibers from various fabrics, cotton, wool, flax from linen, etc., diatoms, scales from insects' wings, and other particles which may occur as dust (see Plate IX, Fig. 6; also Plate X, Fig. 4). Under abnormal conditions the sediment may contain crystalline elements, including uric acid and urates, phosphates, oxalates, cystin, tyrosin, leucin, etc., also organized elements such as epithelium, renal or other casts (Plate IX, Fig. 4), blood globules, pus cells (Plate IX, Fig. 3), spermatozoa (Plate IX, Fig. 2), fat, mucin (Plate IX, Fig. 5), etc. Urinary sediment may be thrown down from a fresh specimen by the use of a centrifuge, or the urine may be

---

* Natural chromate of potash will precipitate copper, the acid chromate precipitates lead only of the second group metals.

allowed to stand in a glass tube with rounded bottom for several hours, when the sediment settles to the bottom by gravity. If possible it is best to examine sediments settled in both of these ways, as the centrifuge will show elements, such as small casts, that would settle slowly, possibly not at all, by the gravity method. On the other hand, the sediment allowed to settle spontaneously will often give a more correct idea of comparative numbers of the various elements observed, than when settled in a centrifuge-tube. A drop or two of formalin may be used to preserve urinary sediment, as suggested on page 327, but if too much of this substance is used, especially in urines containing high percentages of urea, a compound is liable to be formed which has been called formaldehydurea (Plate X, Fig. 5), which settles with the sediment and seriously interferes with the microscopical examination. This compound may form sheaf-like crystals similar to tyrosin and may be mistaken for crystals of sodium oxalate, especially when examined with a low power objective.

Uric Acid. — Uric acid is deposited from normal urine, upon standing, with an excess of free acid (HCl). Urines that have a high degree of acidity will also produce a like deposit, and the finding of uric-acid crystals does not necessarily signify that the crystallization took place within the body, unless special care has been taken that the sample examined was perfectly fresh, although the *tendency* to deposit uric acid is, of course, indicated. The urine from which uric acid separates, as such, is usually rather concentrated and of strong acid reaction. These crystals vary in appearance (Plate X, Figs. 1 and 2), but are almost always colored yellow to red. Colorless crystals are sometimes observed. They are usually quite small, but of the peculiar whetstone shape in which this acid most usually crystallizes. The presence of uric acid has practically no effect upon the acidity of the sample; for, if the acid separates in a crystalline form, it is insoluble, and if it does not separate it is

PLATE X.—URINE.

FIG. 1.
Uric Acid.

FIG. 2.
Uric Acid.
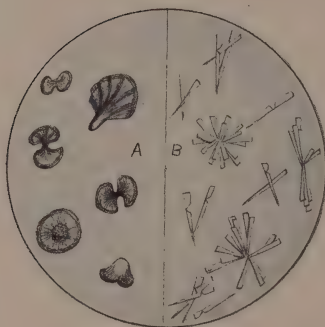
FIG. 3.
A, Sodium Urate; *B*, Sodium Acid Urate.
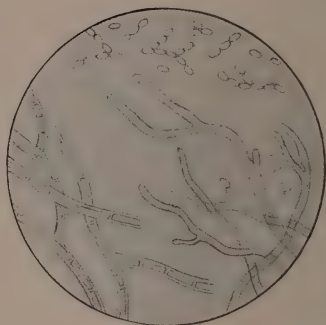
FIG. 4.
Yeast Cells and Molds.
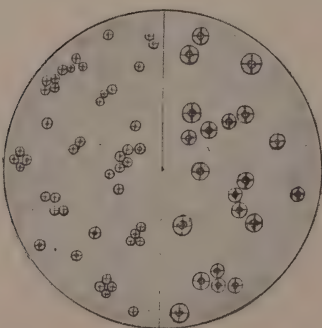
FIG. 5.
Formaldehyd Urea (P. L.).
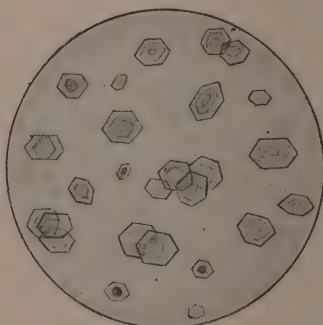
FIG. 6.
Cystin.

in combination as urates, possibly, of course, as acid urates. Uric acid exists normally in proportion to urea as about 1 to 50, but there is no necessary relationship between the quantities of the two substances, and the one may be diminished while the other is increased.

Urates. — Urates may occur as crystalline or amorphous precipitates. The crystalline urates are urate of sodium rarely, acid urate of sodium (Plate X, Fig. 3), and acid ammonium urate (Plate IX, Fig. 1, page 353). The amorphous urates are of the alkaline bases, usually sodium, and are frequently precipitated by lowering of the temperature after the sample has been passed, in such cases the urine assumes a cloudy appearance which is cleared up by the application of heat. A sediment consisting of urates is usually of a pinkish color.

Phosphates. — Phosphates in the urinary sediment may be amorphous or crystalline. They are of the alkaline earths rather than of the alkaline metals, as the latter are soluble in both the acid and neutral forms. The amorphous phosphates deposit with the change of reaction from acid to alkaline, and usually in the form of a so-called triple phosphate of ammonia and magnesia (Plate IV, Fig. 2, page 172). This salt crystallizes in two forms. The prismatic form is the ultimate form; that is, if the crystallization takes place very slowly, the prismatic form is the one in which the salt is thrown out. If it takes place rapidly it may be precipitated in the feathery form, but this slowly changes over to the prismatic form. The acid phosphates may be precipitated closely resembling in appearance the acid urates (Plate X, Fig. 3), but may be distinguished from them by their ready solubility in acetic acid and failure to produce, after solution in acetic acid, any crystals of uric acid such as are obtained from the urates.

Acid Lactates. — These are soluble salts, and are found in urine only by evaporation of a drop of the clear fluid and an examination of the residue by polarized light. When found

in the urine, the significance is quite different from that when found in the saliva, as in the urine they may possibly be formed from lactates, which indicate a faulty action of the liver, and of course they have no connection with tooth erosion. The lactates furnish evidence of similar character.

Oxalates.— Oxalates if found in the sediment usually occur as calcium oxalates. These crystals assume a variety of forms, as shown in Plate II, Fig. 1, page 170. Sodium oxalate (Plate II, Fig. 4) may occur in the urine (not, however, in the sediment), and is detected only by evaporating a drop of the clear liquid and examining with polarized light. Dr. Kirk claims that an oxaluria may be detected in this way for a considerable time before the appearance of the oxalate of lime crystals, and hence such examination becomes a valuable aid to diagnosis. ·

Cystin. — Cystin occurs as six-sided plates. It is a comparatively rare crystal, and indicates insufficient oxidation, particularly of the organic sulphur compounds.

Epithelium.— Epithelium occurs in the urinary sediment from any part of the urinary tract. In the male urine it is much easier to determine the character of the epithelium than in the female, as in the latter the comparatively large amount of mucous surface, from which epithelium may be gathered, furnishes a great variety of forms which are, of course, without clinical significance. The epithelium from the vagina may be quite readily distinguished as very large cells with small nuclei, lying usually in masses overlapping one another but with comparatively slight density. Renal epithelium may be found as small, round cells, differing but slightly in size from a leucocyte. They may be a little larger, a little smaller, or about the same size. They are round and more or less granular in appearance.

Epithelium from the bladder varies considerably, but the majority of cells would properly come under the general head of squamous epithelium, rather large and flat with a distinct nucleus of medium size. Epithelial cells from the neck of the

bladder in male urine are quite typical, being round and comparatively dense with a prominent nucleus. They are four or five times the size of a leucocyte and, in case of irritation at the neck of the bladder, are usually present in considerable numbers and of quite uniform appearance.

Renal casts consist of molds formed within the tubules of the kidneys which retain the form of the tubules after expulsion into the bladder. According to Ogden the most probable theory of their formation is " that they are composed of coagulable elements of blood that have transuded into the renal tubules, through pathologic lesions of the latter, and have there solidified to be later voided with the urine, as molds of the tubules." Casts are termed blood casts, pus casts, epithelial or fat casts according as these elements may adhere with more or less profusion to the cast itself. Pure hyaline casts are pale, perfectly transparent cylinders, with at least one rounded end which can be plainly seen, and may occur occasionally in urine from perfectly healthy individuals. Fibrinous casts are highly refractive and when seen by white light are of a yellowish color and indicate acute and renal disturbance. Waxy casts resemble the fibrinous casts as regards density, but they have no color, and usually indicate advanced and serious stages of kidney disease, while the presence of fibrinous casts has no necessarily serious significance.

Blood and Pus are readily recognized under the microscope after a very little practice. The blood disks are circular and show a characteristic biconcavity in the alternate shading of the edge and center by slight changes of focus. The red corpuscles usually show a shade of color by white light. The pus corpuscles or leucocytes are larger than the red corpuscles, and are granular in appearance. Treatment with acetic acid destroys the granular matter and brings into prominence the cell nuclei, two or three in number. If the leucocytes are free and scattered they should not be regarded as pus but be re-

ported simply as an excess of leucocytes; if they are very numerous and occur in clumps they constitute pus.

Spermatozoa. — Occasional spermatozoa may be found in sediment from either male or female urine and are without clinical significance. If persistent and in considerable numbers, seminal weakness is indicated (Plate IX, Fig. 2, page 353).

Fat occurs in urinary sediment as small globules, highly refractive and varying greatly in size. They are frequently adherent to cells or to casts. Fatty casts indicate a fatty degeneration, which may or may not result from chronic disease. Fat may be demonstrated by staining with osmic acid which is reduced by the double-bonded fatty constituent (olein), leaving a black deposit which stains the globule.

Mucin appears in the sediment as long and more or less indistinct threads. An excessive amount usually indicates irritation of some mucous surface. The source would have to be determined by other more characteristic elements (Plate IX, Fig. 5).

The salts which may be obtained by evaporation of a drop of clear urine and detected by the micropolariscope are similar to those occurring in the saliva; sodium oxalate is probably most frequently found. If the gravity is above normal the urea often crystallizes, making it somewhat difficult to pick out the abnormal crystalline constituents. Phosphates are also usually observed, but these crystals are large and as a rule prismatic, not easily mistaken for anything else.

Recording Results.

As stated at the beginning of the chapter on urine, our object has been the study of this secretion from the standpoint of general metabolism, rather than with a view to differentiate various forms of renal disease, and while it is important that the *presence* of renal disease should be recognized, its further investigation constitutes a proper study for the physician rather

than for the dentist, and when such conditions are found to exist a patient's physician should be apprised of the fact.

Uniformity of method in making out report cards is desirable although not absolutely necessary for the best class work; hence a few suggestions as to the use of the following blank. If no test is made, make no entry whatever on the blank. This permits the use of a dash, " — ", to indicate a diminished (less than normal) quantity. If a substance is present in normal quantity use a capital " N," if increased above normal amount use " +." If absent use abbreviation " abs.," never the dash or minus sign. Observance of this method greatly facilitates correction of the report slips.

U. No.	URINE ANALYSIS BY		
NAME		DATE	
24 h. Am't.		Urea	$\%,=$ Grams in 24 hours.
Sp. Gr.	React.	Uric Ac.	$\%,=$
Color	Appear.	Ammon.	$\%,=$
Ind.	E. Phos.	Chlor.	$\%,=$
Bile	A. Phos.	Phos. Ac.	$\%,=$
Diac. Ac.	Acetone	Sugar	$\%,=$
Alb.		Uric Ac. to Urea $=$ 1 to	
Soluble Salts (cryst.)			
Sediment			

It is often convenient to file analyses by " Case " number. This will always be the same and results of urine analyses, saliva analyses, physical examination of the patient, diet lists and important letters may be brought together forming a complete story of the case.

The following saliva blank has been arranged to facilitate the comparison of quantities of the sulphocyanates and ammonia salts, of albumin and mucin, and of oxidases and nitrites. The common algebraic sign of inequality is serviceable here. $(<, >)$.

S. S.	DATE	NAME	
SALIVA	ANALYSIS FOR		
Appearance	Odor	Acidity	Alkalinity
Specific gravity		Mucin	Albumin
Ammonium Salts		HCNS	Ptyalin
Chlorine		Glycogen test	Phosphates
Acetone		Nitrites	Oxydase
Soluble salts by polarized light			
Viscosity			
Sediment			
REMARKS:			

CHAPTER XL.

METABOLISM.

It has been too much the practice to study a single relation and jump at conclusions without regard to co-relation of factors which may not appear to be closely allied but which nevertheless exert important influences. Witness the effort to establish the relationship of tartar deposition to calcium content of the saliva without considering the quantity of carbon dioxide present or the fact that certain colloidal substances (such as occur in saliva) may prevent precipitation of calcium salts.

The relations of potassium sulphocyanate to dental caries, and other problems have been studied in much the same way, and the object of this chapter is to emphasize the necessity of getting all possible viewpoints of a given question before attempting to draw positive conclusions regarding it.

It is conceded that the general systemic condition may be an important factor in the success of oral treatment by the dentist. In other words it is worth while to know something of the general condition of the patient in addition to the knowledge obtained by the local examination.

Metabolism is an inclusive term indicating the chemical changes whereby the body utilizes the nutritive elements of the food. It may be considered in two divisions as constructive metabolism, anabolism, or synthetic processes, and destructive metabolism, catabolism, or analytic processes.

We have studied the cleavage of complex food molecules as carried on by the digestive processes but they are here by no means complete. How far the cell carries analysis of digestive products is unknown, possibly to very simple forms, but we know that the analytical process is continued and subsequently exten-

sive and complex syntheses result in the building and repair of tissue. The food material upon which tissue building and heat production depend may be classified as of four kinds, Protein, Fat, Carbohydrates, and Mineral Salts.

In considering the utilization of these substances by the system we are obliged to content ourselves with a very general outline and a few definitions. We have suggested the dual nature of metabolism resulting in the maintenance of heat and repair of tissue, but we have come to accept the measure of food value as expressed in terms of heat production alone. This method may not be ideal but as yet we have no unit of value which will measure the usefulness of all four kinds of food material. The unit generally used is the calorie, which may be defined as the degree of heat necessary to raise one kilo of water one degree centigrade, and is a thousand times as great as the small calorie (seldom used).

The combustion of one gram of fat furnishes a heat equivalent of nine and three tenths calories, while a gram of either pure carbohydrate or protein will furnish four calories. These figures are not absolutely accurate because of slight discrepancies between the combustion of metabolism and the combustion of the colorimeter but they are accepted as the basis for computation.

An average adult male doing average work neither wholly sedentary nor wholly muscular will require perhaps 2500 calories per day. This should be made up of a "balanced" diet consisting approximately of eighty grams of protein, one hundred and twenty grams of fat and three hundred grams of carbohydrates. The digestibility and adaptability of food should also receive careful attention, but as this is largely a matter of individual peculiarities tables and rules are impractical. As an illustration of this fact take salt pork and bacon containing similar percentages of fat, and yielding about the same number of calories, but the one is very indigestible, the other is often used in the diet of invalids or small children.

The calorie requirement per kilo of body weight for an adult doing average work is about thirty-five, for children it is much greater than this.

Fat. — The fat molecule does not necessarily undergo decomposition (cleavage) to the same extent as either the protein or carbohydrate molecule; that is, albumin of the egg must be resolved to very simple forms and a new albumin molecule be built up before it can be absorbed and utilized, while fat from one animal can be recovered as such from the tissues of another; the second having used the first for food.

According to Taylor (Digestion and Metabolism) the molecule of stearic acid passes through various acids of the series, the chain splitting each time at the beta carbon till butyric acid is reached. From this point the catabolism proceeds, in part, in the same way as before resulting in formic acid, CO_2 and H_2O, but from butyric acid we may also obtain the beta oxybutyric acid, diacetic acid and acetone. Normal fat metabolism is dependent upon the simultaneous metabolism or combustion of carbohydrates, that is, the absence of carbohydrates results in acidosis due to imperfect oxidation of fat and consequent formation of the acetone bodies.

Protein metabolism results in the splitting of the complex protein molecule with the formation of amino acids. Some of these such as glycerol, alanin and aspartic acid are capable of producing carbohydrates, others like tyrosin and histidin are not. The cleavage of some amino acids splits off urea, but in a much larger number of cases such cleavage results in the formation of ammonia which then unites with water and carbon dioxide forming urea.

Carbohydrates. — The present concept of carbohydrate metabolism is given by Dr. Percy G. Stiles in the Boston Medical and Surgical Journal for April, 1917. From this article we abstract the following brief conclusions:

Carbohydrates after digestion and absorption are found in

the blood stream as blood sugar (glucose). This sugar is oxidized by the muscles, resulting in the production of lactic acid, the presence of which causes fatigue. During relaxation this lactic acid is reincorporated in an undetermined "precursor" which had been responsible for its production in the first place.

Concerning the rôle of the pancreas in carbohydrate metabolism Stiles says, "A function of this organ even more necessary than its digestive contribution is the delivery to the blood of the hormone which makes it possible for the muscles, including the heart, to oxidize sugar. Abundance of this hormone insures a high tolerance for sugar; want of it produces, according to the degree of the lack, a low tolerance or substantial inability to make use of carbohydrate."

Mineral Salts. — A well-balanced diet will furnish the proper amounts of mineral solids (excepting perhaps sodium chloride) but all diets are not balanced and it is well to know what part the various salts have in maintaining the health of the individual.

Sodium chloride is essential to digestion because it has been repeatedly demonstrated that if sodium chloride is withheld hydrochloric acid will not enter the stomach. Excess of sodium chloride may cause irritation or place an undue strain upon weak or diseased kidneys and in such cases should be avoided; on the other hand acidosis usually results from a salt-free diet.

Potassium salts are said to keep the tissues soft and pliable, to prevent hardening of the arteries, etc., but potassium salts may cause a diminution of necessary sodium according to Bunge (Physiologic and Pathologic Chemistry, 2nd Edition), who says that potassium salts will react with sodium chloride in the system forming potassium chloride and undesirable sodium salts, both of which are eliminated by the kidneys and thus cause loss of sodium.

Tibbles quotes Cahn in Zeit. f. Physiol. Chem. in practically the same statement.

Calcium salts in considerable quantities are essential during

childhood and in fact as long as calcification of any sort is a necessary process (as in pregnancy). In old age the system needs but little calcium. Tibbles says that daily diet should include one to one and one-half grams of calcium oxide, and care should be taken that it is not lost as oxalate.

H. C. Hartwig in the International Journal of Orthodontia finds a direct relationship between the calcium content of the saliva and caries in pregnant women. Cosmos 1917, page 665.

Magnesium occurs generally distributed in the system, the bones containing about one per cent. By increasing the amount of magnesium ingested the percentage in the bone may be increased but it does not take the place of calcium. The compounds of magnesium are generally more soluble than those of calcium. Magnesium oxide, as milk of magnesia, is used extensively as an antacid. An excessive amount, however, may act in removing necessary calcium in just the same way that potassium acts in removing sodium, as indicated by the following from Pickerills' Prevention of Dental Caries and Oral Sepsis, page 120.

"Weiske's experiments also support these findings. For instance, of two rabbits, one received one gram $CaCO_3$ daily in addition to its food; the other one gram of $MgCO_3$ for three months. The rabbits were then killed, and it was found that, although they were of equal body-weight, the total weight of the bones (dried and fat-free) in the first rabbit exceeded that of the second rabbit (77.45 grams : 69.52 grams); and, further, that the amount of organic matter in the bones of the $MgCO_3$ rabbit was in excess of that in the $CaCO_3$ rabbit."

Iron is an essential constituent of blood derived from food, and perhaps more than in the case of any other mineral constituent, it is necessary for iron to be taken in natural organic combination.

Phosphates are essential for the development of all cellular tissue. Phosphates are credited with preventing the deposition of uric acid by the reaction on page 242, also with keeping

calcium oxalate in solution.   Phosphate acts beneficially in the bowels by slightly stimulating the peristaltic action.

Iodine occurs in the ductless glands, and is apparently necessary for their best development, although this fact has been seriously questioned.

It is impracticable to give tables of food composition, but the following may be noted:

Strawberries, beans and potatoes are rich in potassium compounds; beets, spinach, turnips and cherries are rich in sodium salts; milk, oranges, turnips and parsnips are rich in calcium oxide; almonds and walnuts are rich in mangesium oxide; carrots and rice are rich in iron; meat, cheese, beans, eggs and wheat are rich in phosphates; coca powders, rhubarb, and spinach, are rich in oxalates.

Vitamines. — In regard to these substances we quote again from Doctor Stiles: "Five years ago the emphasis in this sphere (the field of nutrition) was upon the variable value of proteins from different sources.   It appears largely to have shifted to the importance of minor constituents of the diet.   The view that beriberi, scurvy, and perhaps pellagra are deficiency diseases, in the sense that they are caused by the failure of the food to provide certain specific compounds which are required for normal maintenance, is generally familiar.   It was at first proposed to describe these essential substances as vitamines.   The term would imply that they were nitrogenous and of a fixed molecular type.   It has been thought better to call them merely accessory substances.   This does not commit one to any narrow conception of their chemical nature."

EXPERIMENTS.

IF possible it is highly desirable to spend a little time in reviewing the principles which form a necessary foundation for any kind of chemical specialization. These are supposed to have been studied in High School course, but in the author's experience many students enter upon the study of dentistry not directly from High School graduation but after a lapse of one, two, or more years. Hence a few experiments are introduced suitable to accompany such a lecture review as suggested above.

Oxidation and Valence.

Exp. 1. Weigh carefully a porcelain crucible. Then weigh into it about one gram of clean copper turnings. Heat strongly for about fifteen minutes; then cool and weigh. Explain increase of weight and compare result obtained with theoretical result, assuming that the entire amount of copper had been oxidized.

Exp. 2. To a solution of potassium chlorate add a little sulphurous acid and boil. Test the sulphurous acid for sulphuric acid (H_2SO_4) before starting and after completing the experiment.

Exp. 3. Prepare some chlorine water as follows: Into a test-tube drop some crystals of $KClO_3$. Add a few c.c. of strong HCl, just enough to cover the crystals. Allow the evolution of gas to become fairly brisk and fill tube three-quarters full of water.

$$KClO_3 + 2\,HCl = KCl + Cl + ClO_2 + H_2O.$$

CAUTION. Avoid heating, as in this reaction oxides of chlorine are formed which are liable to explode if heated.

Avoid the escape of Cl gas into the laboratory as far as possible.

Exp. 4. Warm a little sulphurous acid solution with a few drops of the chlorine water just prepared, testing for H_2SO_4 as in Exp. 2.

Exp. 5. To a dilute solution of potassium ferrocyanide add some strong chlorine water, and warm. After ten or fifteen minutes test for the presence of ferrocyanide with dilute ferric chloride. Explain.

Crystallization and Solution.

Exp. 6. Make hot, nearly saturated solutions of each of the following: potassium bichromate, sodium chloride, potassium nitrate. Turn off, or filter, the clear, hot solutions and allow to cool. When they have nearly reached the room temperature, again decant the clear solutions and place in ice water until thoroughly cold. Compare the effects of the temperature on the solutions of the three salts.

Exp. 7. Wrap a few crystals of $KMnO_4$ in a piece of filter paper and suspend in the top of a test tube-full of water. Inference regarding gravity of solution?

Exp. 8. Mix equal volumes of ether and water in a test-tube. Shake gently, allow to separate completely. Remove a portion of the ether and test for water with anhydrous $CuSO_4$.

Exp. 9. Into the 25 c.c. graduate in your desk, measure as accurately as possible 15 c.c. of alcohol. Into a second graduate measure in like manner 10 c.c. of water and add it slowly to the alcohol in the first graduate. Stir carefully with a glass rod. Note change in temperature if any. Note volume of mixed liquids and explain.

Exp. 10. In a test-tube dissolve a small crystal of iodine in one or two cubic centimeters of alcohol. Note color of solution. Add ten cubic centimeters of water and explain appearance of the iodine solution. Now add five to ten cubic centimeters of

chloroform, close tube with thumb and turn over several times. Explain results.

Osmosis and Dialysis.

Exp. 11. The student may satisfactorily demonstrate osmotic pressure for himself by the use of the following experiment:

Prepare a substitute for the usual semipermeable cup by taking the ordinary dialyser parchment tubing. Soak first in warm water and then in a dilute solution (2%) of potassium ferrocyanide. Allow to become nearly dry and then soak in a dilute solution of copper sulphate. Allow the tube to become nearly dry again, then wash once or twice with warm water.

With dialyser tubing thus prepared, a small bag or pouch capable of holding 10 or 15 c.c. can be made and tied very tightly to one end of a piece of glass tubing four or five inches long with an internal diameter of three or four millimeters.

Fill the parchment bag with sugar solution and then introduce a previously selected capillary tube which fits into the larger tube rather closely. Seal joints A and B (Fig. 33) with paraffin and suspend the bag in a beaker of distilled water. Watch the level of the liquid in the capillary tube.

Exp. 12. In a dialyzing tube (Fig. 26, page 316) place a solution of NaCl. In another dialyzing tube place a solution of egg albumin; set the tubes in separate small beakers of distilled water. After several hours standing test the distilled water in the first beaker for salt by adding a little silver nitrate solution, and test the water in the second beaker for albumin by boiling with a drop of acetic acid. Compare results of these tests with similar tests made with known solutions of salt and of albumin.
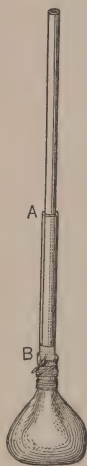
FIG. 33.

Neutralization and Hydrolysis.

Exp. 13. Add a dilute solution of caustic potash to 5 c.c. of nitric acid diluted with twice its bulk of water, until the mixture turns litmus paper neither red nor blue. WITHOUT boiling evaporate the solution in a porcelain dish. Test with glass rod until a drop hardens as it cools, and becomes almost solid. Then let entire solution become cold.

Note three differences in the substance produced by this experiment from either of the original substances used.

Write in your laboratory notebook the following neutralization reactions:

1. Ammonium hydroxide and nitric acid.
2. Sodium hydroxide and nitric acid.
3. Ammonium hydroxide and oxalic acid.
4. Sodium hydroxide and oxalic acid.
5. Sodium hydroxide and nitrous acid.

Exp. 14. Röse's Reaction.* — Color a solution of borax, ($M/10$) with litmus solution, then add acetic acid very carefully till the litmus just turns pink. Now dilute largely by turning into distilled water when the color again becomes blue due to increased hydrolyzation of the borax.

Exp. 15. Place 2 c.c. of $M/10$ solution of borax in each of two small beakers, add to one a few drops of $HgNO_3$, and to the other a few drops of $AgNO_3$ solution. Note the color of the precipitate in each case.

In each of two larger beakers place 50 c.c. of water with five or six drops ($1/2$ c.c.) of the above borax solution, then to one add a few drops of $HgNO_3$ solution, and to the other some $AgNO_3$ solution till a precipitate is produced. Note color of precipitate in each case (Hg_2O and Ag_2O are produced).

Now dilute the mixture in the first two beakers (containing precipitate of borates) with 50 c.c. of water. Stir and allow to

* Holleman-Cooper, Inorganic Chemistry.

stand ten minutes. Draw inference regarding hydrolysis of borax, also regarding relative stability of the borates of silver and mercury.

Equilibrium and Ionization.

Exp. 16. To 5 c.c. of a tenth molar solution of ferric chloride add 15 c.c. of a tenth molar solution of KCNS. Dilute a portion of the red solution thus produced with distilled water until only a faint yellow color remains. Divide this nearly colorless solution into four parts. To one add 2 or 3 c.c. of ferric chloride, to the second, about twice as much of the KCNS originally used, to the third, add one-half its volume of M/10 solution of KCl.

Compare portions 1 and 2 and explain how this experiment shows the law of chemical equilibrium.

Explain also how it illustrates ionization of ferric sulpho-cyanate and why it is necessary to use more of the KCNS than of the $FeCl_3$ solution to get approximately the same depth of color.

Now compare 3 and 4 and explain how these solutions show the reversible character of the reaction between $FeCl_3$ and KCNS. Do portions 3 and 4 illustrate law of mass action?

Peroxides.

Exp. 17. Prepare a solution of peroxide of hydrogen as follows: Add to 10 or 15 grams of BaO_2 enough water to make a paste and allow to stand about half an hour. Then add 20 or 30 c.c. of a ten per cent. solution of H_2SO_4. Stir thoroughly and after five minutes filter off the solution and test for H_2O_2. (Test given on page 181.)

The half hour treatment with water serves to hydrate the BaO_2 and makes the action of the acid much more rapid.

What is the white solid remaining on the filter paper?

Complete $BaO_2 + H_2SO_4 =$

Exp. 18. Dissolve peroxide of sodium in dilute HCl leaving the reaction faintly acid. Dissolve also a little peroxide of

sodium in water and compare the bleaching properties of the two solutions.

Exp. 19.   To a solution of H_2O_2 add a little KI solution, then add about 5 c.c. of chloroform.   Shake well.   Set aside for a few moments then examine and explain result.

Exp. 20.   Dissolve a very little sodium perborate, $NaBO_3$.- $4 H_2O$, in a little *warm* water and test the solution for H_2O_2 with potassium bichromate, sulphuric acid and ether as on page 181.

LABORATORY WORK IN QUALITATIVE ANALYSIS.

During the study of qualitative analysis the preliminary work for each group, which may consist in confirming the statements given in the text regarding the formation of precipitates and properties of the same, should be carried out prior to the analyses of unknown solutions.   In addition the following experiments may be used.

Experiments with metals of Groups I and II.

Exp. 21.   Precipitate a little silver chloride according to the following:

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

Filter and allow the precipitate to become nearly dry.   Mix a little of the precipitate with powdered charcoal, and heat before the blowpipe until a globule of metallic silver is obtained.

Exp. 22.   Mix intimately a small quantity of litharge and powdered charcoal.   Heat in a blowpipe flame and obtain a particle of metallic lead.

Exp. 23.   In a solution of lead (acetate or nitrate) suspend a strip of zinc.   Set aside for several hours and note the separation of metallic lead.   Write the reaction.

Exp. 24.   Put a small quantity of cinnabar (HgS) into a small, hard glass tube open at both ends.   Hold the tube, slightly inclined, in a strong heat of the Bunsen flame; then examine the sublimate under the microscope.   What becomes of the sulphur?

Exp. 25. Hold a strip of iron or steel (knife blade) for a few seconds in a solution of copper sulphate. Does the strip of iron dissolve? If so, in what combination?

Exp. 26. In an open, hard glass tube, heat strongly a mixture of charcoal and copper oxide. Explain the change of color.

Exp. 27. To a very small piece of copper foil in a test-tube, add a little ammonium chloride solution and allow to stand.

Aluminium, Chromium, and Iron.

Exp. 28. (*a*) To 5 c.c. of dilute alum solution containing a little NH_4Cl, add NH_4OH solution and heat.

Note. — NH_4Cl aids in the complete separation of the $Al_2(OH)_6$.

Write reaction. Will the precipitate dissolve in an excess of the reagent?

(*b*) Repeat, using a chromium solution in place of the alum.

Exp. 29. Prepare cobalt aluminate according to directions given on page 59. This should result in a fine blue color; two or three trials may be necessary to produce result.

Exp. 30. Dissolve a few crystals of $FeSO_4$ in water. Filter, if necessary, and to a portion of the clear solution add a little ammonia water. To another portion add a few drops of HNO_3 and boil for two or three minutes. Carefully add ammonia water till a permanent precipitate is obtained.

To a solution of ferric alum add a little ammonia. What change is produced by the HNO_3 in the second part of the experiment?

$$FeSO_4 + NH_4OH = ?$$
$$3\ H_2SO_4 + 6\ FeSO_4 + 2\ HNO_3 = ?$$
$$Fe_2(SO_4)_3 + NH_4OH = ?$$

Note. — The addition of sulphuric acid is not necessary to the oxidation by HNO_3. It simplifies the reaction, as otherwise more or less ferric nitrate is formed.

Exp. 31. Make a little fresh solution of potassium ferricyanide, also a solution of ferrous sulphate; to the latter add a little H_2SO_4 and a piece of iron wire. After hydrogen ceases to

be evolved make the following tests, completing the reaction in each case:

$$FeSO_4 + K_3FeCy_6 = ? \qquad Fe_2Cl_6 + K_3FeCy_6 = ?$$
$$FeSO_4 + K_4FeCy_6 = ? \qquad Fe_2Cl_6 + K_4FeCy_6 = ?$$
$$FeSO_4 + KCNS = ? \qquad Fe_2Cl_6 + KCNS = ?$$
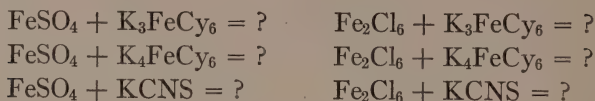
Exp. 32. To a solution of chrome alum add a little NH_4OH. Filter, wash the precipitate once or twice and allow to dry.

$$Cr_2(SO_4)_3 + NH_4OH = ?$$

To this dried precipitate add a little dry sodium carbonate and potassium nitrate. Mix thoroughly, transfer to a porcelain crucible and heat strongly for several minutes, cool and note the color of the fused mass. Dissolve in water, acidify with acetic acid, and divide the solution into two parts; to the first add a few drops of a solution of $Pb(NO_3)_2$ or $Pb(C_2H_3O_2)_2$, and to the second a few drops of $BaCl_2$.

Cobalt, Manganese, Nickel, and Zinc.

Exp. 33. Add to solutions of $Co(NO_3)_2$, $MnSO_4$, $Ni(NO_3)_2$, and $ZnSO_4$ a few drops of $(NH_4)_2S$ solution.

Note color of precipitate and write reaction in each case.

Exp. 34. On four separate filter papers collect the several precipitates formed in Exp. 33. Wash once with H_2O and make a borax-bead test with each precipitate as shown in the laboratory demonstration. To each precipitate add, on the paper, cold dilute HCl.

Exp. 35. (a) To a solution of $ZnSO_4$ add a little NH_4OH. Will the precipitate dissolve in excess of reagent?

(b) Repeat, adding NH_4Cl before using the NH_4OH.

(c) Repeat (a) using NaOH in place of NH_4OH.

Exp. 36. Precipitate a little MnS, filter and wash. Make red-lead test as described at bottom of page 63.

Exp. 37. (a) To a solution of $Co(NO_3)_2$ in a test-tube, add

a drop or two of dilute NH_4OH. Now add an excess of NH_4OH and note if any change occurs.

(*b*) Repeat, using a solution of $NiSO_4$.

What are the precipitates formed?

Exp. 38. To a solution of zinc salt add a solution of Na_2CO_3. The precipitate is a basic carbonate of zinc.

Balance the equation

$$ZnSO_4 + Na_2CO_3 + H_2O = Zn_5(OH)_6(CO_3)_2 + Na_2SO_4 + CO_2.$$
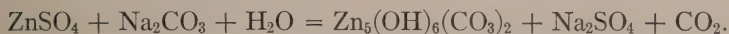
Exp. 39. Shake in a test-tube a little ZnO and water, filter and test filtrate for Zn as in Exp. 33.

Repeat using ammonium chloride solution instead of the water. Inference.

The Alkaline Earths.

Exp. 40. To a little clear lime water add a few drops of ammonium carbonate solution.

$$CaO_2H_2 + (NH_4)_2CO_3 = ?$$

Will an excess of reagent dissolve this precipitate? If CO_2 were used in place of $(NH_4)_2CO_3$ would the solubility of the precipitate be the same? Why?

Exp. 41. Take in separate test-tubes about 5 c.c. of each of the following dilute solutions: $CaCl_2$, $BaCl_2$, $Sr(NO_3)_2$, and $MgCl_2$. Add to each 1 or 2 c.c. of NH_4Cl solution, and then a little $(NH_4)_2CO_3$ solution.

Now add cautiously to each tube, containing a precipitate, dilute acetic acid till the precipitates are all dissolved. To each of these three tubes add a few drops of $K_2Cr_2O_7$ solution.

Write the reactions. Formulate a method for the separation of Ca, Ba, and Mg from a mixture containing all three.

Exp. 42. To a solution of magnesium chloride add a little NH_4OH and NH_4Cl solution and lastly some sodium phosphate.

The formula for the precipitate is NH_4MgPO_4. Complete the reaction.

$$MgCl_2 + Na_2HPO_4 + NH_4OH =$$

Exp. 43.   To each of the four solutions used in Exp. 41 add a little dilute H_2SO_4.

Which of the four metals forms the least soluble sulphate?

Which the most soluble?

Exp. 44.   To a solution of $Sr(NO_3)_2$ add a solution of $CaSO_4$ and allow to stand.

Exp. 45.   To a solution of a calcium salt add some ammonium oxalate solution.   Write reaction.

Exp. 46.   In a watch glass place a few drops of lime water, in another place some baryta water.   Set the two glasses aside for a while and explain any change that takes place.

Exp. 47.   Make flame tests with solutions of barium, strontium and calcium.

The Alkali Metals.

Exp. 48.   In 10 or 15 c.c. of water contained in a porcelain dish, dissolve a small piece of metallic potassium.

Stand well away from the dish as the reaction may result in spattering hot water or hot metal.

Test resulting solution with red litmus paper.*   Write reaction.

Exp. 49.   Take a little strong solution of carbonate of soda (about 20% of crystallized salt), heat nearly to boiling in a porcelain dish, then add about half as much milk of lime (made of one part $Ca(OH)_2$ to four parts water).   Continue the boiling for several minutes, then allow to settle.   Decant the clear liquid.

Test the liquid with various indicators.   Is it acid or alkaline?

To a small portion of it add a few drops of HCl.   Does it effervesce?   Test in a similar manner the carbonate of soda solution,

$$Na_2CO_3 + CaH_2O_2 = ?$$

* Blue paper may be reddened by leaving it a few hours in a wide-mouth bottle after wetting the under side of the stopper with a drop or two of acetic acid

Which of these two compounds used is a base?

Which an alkali?

Exp. 50. In separate test-tubes heat the following mixtures:

1. Solution of NH_4Cl and solution of $NaOH$.
2. Solution of $(NH_4)_2SO_4$ and solution of KOH.
3. Dry NH_4Cl and dry CaO_2H_2.

In each case note the odor of the gas evolved and test the VAPOR with moistened red litmus paper and write the reaction.

Exp. 51. Take three test-tubes and into one put about 5 c.c. of a dilute solution $NaCl$; into the second, KCl; and into the third, NH_4Cl; then to each add a few drops of platinic chloride solution and allow to stand till the next exercise.

Exp. 52. Make flame tests according to directions given in the lecture room, with salts of sodium, potassium, and lithium.

Exp. 53. Place in an ignition tube one or two grams of potassium tartrate and heat till no further change takes place. Cool and dissolve in water. Test a portion of the resulting solution with a few drops of HCl. In like manner test the original tartrate.

Note. — In general, the ignition of salts of organic acids results in the formation of carbonates.

Exp. 54. Make a spectroscopic examination of solutions of Na, K, Li, Ba, Sr, and Ca, and describe the bands observed.

Note. — This experiment is only to be performed under the direction of an instructor. Opportunity will be given for this experiment during the next exercise if necessary.

EXPERIMENTS FOR CHAPTER XI.

Exp. 55. Heat in forceps or on triangle a very small piece of each of the following metals, allowing each to fall as it melts onto a smooth cold slab (cement floor will do). Return melted metals to office for credit.

Ni–Fe–Cu–Mg–Zn–Cd–Bi–Sn.

Study table of melting-points and write your conclusions regarding the temperature of the Bunsen flame.

Exp. 56. Fill each of three test-tubes half full of a solution of $CuSO_4$. Suspend in the first a knife blade; in the second, a strip of clean metallic zinc; in the third, a strip of magnesium ribbon. Write reactions.

Exp. 57. Warm gently in a test-tube a little MnO_2 and HCl. Write reactions. Repeat with PbO_2 and HCl; with PbO and HCl. Explain differences in action of the metallic oxides.

EXPERIMENTS FOR CHAPTERS XII–XIV.

During the study of Chapters XII–XIV inclusive, the student will be required to make qualitative analyses of several commercial alloys, dental cements, etc. He will also have to prepare and test carefully six alloys, the formulæ for which will be given on a mimeograph sheet similar to that represented on page 379.

The properties of the various alloys are to be carefully compared and it is often desirable for two or more students to vary a given formula in some one particular and note the result of such a variation upon the properties of the amalgam obtained.

ALLOYS.

Date...............

Desk No......... Name..

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
Gold.........						
Silver........			18	60	55	
Tin...........	3	1	65	40	37	
Copper.......					4	
Zinc..........					4	
Lead.........	5	2				
Antimony.....			17			
Bismuth.......	8	4				
Cadmium......		1				

Nos. 1 and 2 contain lead and must not under any circumstances be made in the graphite crucible which you intend to use for silver-tin alloys. These are solders or fusible metals. Make 8 to 10 grams and determine melting-point of each.

No. 3 is a very low grade dental alloy. Make 10 grams and test for expansion, discoloration, and crushing strength.

Nos. 4 and 5 are better grade alloys. Make 10 or 12 grams of each. Hand one in as sample of work; test the other, annealed and unannealed, as No. 3 was tested.

No. 6, your own formula. Make 15 to 20 grams. Make complete tests and also return sample. Return all remaining portions of alloys with desk number and composition of the alloy plainly written on envelopes furnished, in order to obtain proper credit for the work.

CHAPTER XV.

As part of the work in studying dental cements the student is expected to make a mixture of pure zinc oxide and sirupy phosphoric acid; then to study the modification of the properties of the resulting cement by various additions of insoluble phosphates and magnesium oxide to the acid or powder. He is also expected to make qualitative analyses of two commercial cements one of which shall be a copper cement.

CHAPTER XVII.

Standard solutions are prepared illustrating volumetric processes by neutralization, oxidation and precipitation. Numerous unknown quantitative solutions are given each student for practice.

CHAPTERS XIX AND XX.

In the study of substances commonly used in dental preparations the simpler tests are regarded as important; these have been included in the text. If time permits the analysis of a few unknown anesthetics, mouth washes and powders will aid materially in fixing the composition of this class of substances in the student's mind.

If material is available the analysis of various forms of tartar is especially instructive. It will be necessary to use the microchemical methods suggested in Chapter XVIII for this work.

ORGANIC CHEMISTRY.

Experiments with Carbon and Hydrocarbons.

Exp. 58. Carbon as a decolorizing agent. To 25 or 30 c.c. of a dilute solution of aniline color, contained in a small beaker, add a teaspoonful of bone charcoal. Heat to the boiling-point, rotate or stir thoroughly for a few minutes, and filter.

Exp. 59. Absorption of metallic salts. To 25 c.c. of solu-

tion of lead acetate of such strength that H₂S water gives marked color but no precipitate, add a teaspoonful of bone charcoal and treat as in preceding experiment. Test the filtrate with H₂S water and note whether lead has been removed.

Exp. 60. Perform an experiment with a view to determining whether bone charcoal will absorb H₂S from H₂S water.

Exp. 61. Repeat either of the three immediately preceding experiments, using wood charcoal in place of bone charcoal. Does the wood charcoal work as well as the bone charcoal in the absorption of color or other substances? How does bone charcoal differ in composition from wood charcoal?

Exp. 62. Arrange apparatus as shown in Fig. 34. To the boiling flask (*B*) provided with a thermometer registering 200° C.
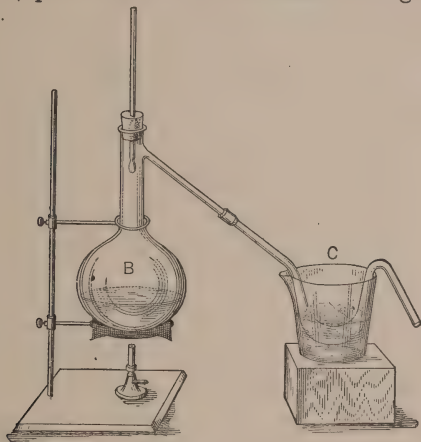
Fig. 34.

connect a beaker condenser, *C*, immersed in ice water. In this apparatus distil slowly 25 c.c. of crude petroleum until at least four fractional products are obtained, with boiling points differing by at least 15°. Compare the physical properties of the distillates thus obtained.

Exp. 63. Charge an ignition tube with dry "marsh-gas mixture," found on side shelf (consisting of NaC₂H₃O₂, NaOH,

and CaO_2H_2). Fit with a delivery tube and collect two small bottles of the gas over water.

$$NaC_2H_3O_2 + NaOH = CH_4 + Na_2CO_3.$$

Test the inflammability of this gas. Notice the odor.

Exp. 64. Mix carefully in a test-tube 2 c.c. of alcohol and 8 c.c. of strong sulphuric acid. Heat gently and notice odor of gas. Fit a bent glass tube to the test-tube and collect over water a test-tube full of the gas. To this apply a flame. Note the color of the burning gas.

$$C_2H_5OH - H_2O = C_2H_4.$$

Exp. 65. Collect a test-tube full of ethylene (Exp. 64), add a few c.c. of dilute permanganate solution and shake. Then repeat, using Marsh gas in place of the ethylene (test for unsaturated hydrocarbons).

Exp. 66. Shake together, in separate test-tubes, small quantities of petroleum and sulphuric acid in one tube, and petroleum and nitric acid in the other. If no action results, mix contents of the two tubes and shake again. Explain any change or absence of change which may be apparent.

Exp. 67. In a small generator (see model) place a few small pieces of calcium carbide (CaC_2), add strong alcohol through the funnel tube till the lower end of the tube is "sealed." Now add very slowly a little water till a brisk evolution of gas is obtained. Collect over water two or three test-tubes full of the gas. (Acetylene.)

Test with a lighted splinter. Note odor of gas cautiously, as it is poisonous when inhaled in quantity.

$$CaC_2 + 2\,H_2O = Ca(OH)_2 + C_2H_2.$$
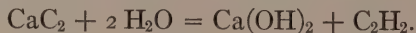
Exp. 68. Conduct a little of the acetylene gas into an ammoniacal cuprous chloride solution.* What is the red precipitate?

* See appendix for preparation of reagent. This test is characteristic of the triple-bonded hydrocarbons.

Exp. 69. If the evolution of gas (Exp. 68) has not been interrupted the delivery tube may be replaced by a short tube drawn out to a fine point and the gas ignited. Note color of flame. If it smokes badly, explain the reason for it.

Experiments with the Halogen Derivatives of the Hydrocarbons.

Exp. 70. Place in a test-tube a little bleaching-powder, cover with strong alcohol and heat the mixture to boiling. Notice carefully the odor of the vapor produced and compare with a little chloroform ($CHCl_3$) from side shelf.

$$4 \, C_2H_5OH + 8 \, Ca(ClO)_2 = 2 \, CHCl_3 + 3 \, \underset{\text{(Formate of Ca)}}{Ca(CHO_2)_2}$$
$$+ \, 5 \, CaCl_2 + 8 \, H_2O.$$
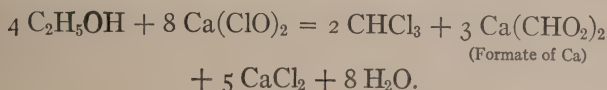
Exp. 71. Heat 1 c.c. of chloroform with about 5 c.c. of one per cent NaOH. Test a portion of the resulting solution for inorganic chlorides. Distil the remainder of the solution and test the distillate, collected in a test-tube, with litmus paper.

Exp. 72. Place in a test-tube about 1 gram of crystallized carbonate of sodium, about half as much iodine and 1 or 2 c.c. of alcohol. Now add 10 or 15 c.c. of H_2O and keep the mixture at moderate heat (not boiling) till the color of the iodine is discharged. Allow to cool; collect on a small filter paper some of the yellow crystals which have been formed and examine under the microscope. What are the crystals? Explain their relation to marsh-gas.

Exp. 73. Prepare ethyl bromide from alcohol, potassium bromide and sulphuric acid as follows: Using the apparatus suggested for experiment 62, place in the distilling flask about 30 c.c. of 50% alcohol. Add slowly with constant agitation 30 c.c. of strong sulphuric acid. Cool thoroughly, then add 30 grams of powdered potassium bromide. Distil carefully until condenser is nearly full of distillate. Pour about a quarter of the product into excess of water. Shake well to wash the ethyl

bromide. Remove from the wash water by means of a pipette and dissolve in a little alcohol. Test this alcoholic solution for bromine with alcoholic silver nitrate.

To another portion of the ethyl bromide add 5 to 10 c.c. of alcoholic potassium hydroxide (5% in absolute alcohol). Boil for a minute or two, dilute with water and make the usual qualitative test for bromides.

Write reactions.

Ethyl bromide may also be prepared by distilling a mixture of one part of alcohol and five parts of strong hydrobromic acid.

Exp. 74. Cover one or two small pieces of calcium carbide, in a small porcelain dish, with a mixture of three parts water and one part alcohol. While the gas is being evolved hold over the mixture a test-tube full of chlorine.

Experiments with Alcohols. (*Chap. XXII.*)

Exp. 75. The detection of water in alcohol. Prepare a little anhydrous copper sulphate by heating a few crystals of $CuSO_4$ on a crucible cover until the water is driven off and a nearly white powder results. If this white powder is added to half a test-tube full of alcohol, the absorption of water, if present, will result in reforming the crystallized salt and a consequent production of blue color.

Exp. 76. Water may be separated from alcohol by saturating with potassium carbonate. To demonstrate this, take a mixture of alcohol and water, containing fifteen or twenty per cent of alcohol, and add solid potassium carbonate until the salt will no longer dissolve. Agitate and allow to stand. Two layers will form, one consisting of alcohol, the other of the water solution of K_2CO_3.

Exp. 77. To about 75 c.c. of a 10% glucose solution add a little yeast and allow to stand for twenty-four hours at a temperature of about 37° C.; then distil by means of gentle heat 10 or 15 c.c., and test distillate for alcohol by iodoform test,

as given on page 383, Exp. 72. The production of CO_2 may also be demonstrated if the gases evolved during the fermentation are passed into clear lime water:

$$C_6H_{12}O_6 = 2\ C_2H_5OH + 2\ CO_2.$$

Exp. 78. A test for methyl alcohol. This test is applicable only to slight traces of methyl alcohol and may be made with a one to two per cent solution or with the first cubic centimeter of distillate from the substance suspected of containing methyl alcohol. Place 2 or 3 c.c. of very dilute methyl alcohol in a test-tube, heat a spiral of copper wire to white heat in a Bunsen flame and plunge immediately into the solution to be tested. Cool the contents of the tube by immersion in freezing mixture or ice water, and repeat the treatment with the hot copper wire. Cool again, and a third time introduce the hot copper wire. The copper spiral can be made by winding copper wire around a lead pencil, and should be of such a length that it is not wholly covered by the liquid in the tube.

This process serves to oxidize a portion of the alcohol to aldehyde. Now add to the solution which is being tested a few drops of a 1/2% water solution of resorcinol and underlay the mixture with strong sulphuric acid. A violet ring will indicate the presence of methyl alcohol. The higher alcohols will give red or brown rings when similarly treated.

Exp. 79. Repeat experiment 78, using ethyl alcohol in place of methyl alcohol.

Exp. 80. In 5 or 10 c.c. of absolute alcohol dissolve 1/4 to 1/2 gram of metallic sodium. Test the gas given off.

Write reaction. Save the product.

Exp. 81. Repeat Exp. 57, using allyl alcohol instead of ordinary alcohol.

Experiments with Aldehydes and Ketones. (Chap. XXII.)

Exp. 82. Mix about 1 c.c. of a very dilute solution of formaldehyde with four or five times its volume of milk in a test-

tube.   Keep at a temperature of 40 to 50° C. for half an hour, then carefully underlay the mixture with commercial sulphuric acid of a specific gravity of 1.80.   At the point of contact of the two layers of liquid a violet-colored ring indicates the presence of formaldehyde.   It is necessary that time be allowed for the casein of the milk to unite with the formaldehyde, also that the sulphuric acid should contain a trace of iron; this the *commercial* acid usually does.   It is undesirable that the acid should be stronger than of 1.80 specific gravity; for, if it is, a *reddish-brown* ring may be formed, due to partial carbonization of the casein.

Exp. 83.   To a very dilute solution of formaldehyde add a few drops of 1/2% resorcinol solution and underlay the mixture with H_2SO_4 as in Exp. 78.   The appearance of a violet ring will constitute a test for formaldehyde.

Exp. 84.   To about 5 c.c. of a *strong* aqueous solution of potassium dichromate add a little sulphuric acid, then a few cubic centimeters of alcohol, and notice the odor of acetaldehyde produced by oxidation of the alcohol.   Note also the reduction of the dichromate to $Cr_2(SO_4)_3$, as follows:

$$K_2Cr_2O_7 + 4\,H_2SO_4 + 3\,C_2H_5OH =$$
$$K_2SO_4 + Cr_2(SO_4)_3 + 3\,C_2H_4O + 7\,H_2O.$$
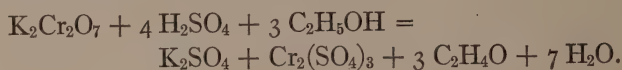
Exp. 85.   Test dilute solutions of acetone, formic and acetic aldehydes by Tollen's test for aldehyde as follows: Into a clean test-tube which has been rinsed with NaOH solution, place 5 c.c. of Tollen's reagent, add 10 c.c. of solution to be tested, shake; the silver is reduced, forming a metallic mirror on the inner surface of the tube.

To make Tollen's reagent, dissolve three grams of silver nitrate in 30 c.c. ammonia water and add 3 c.c. of solution of sodium hydroxide.

Exp. 86.   Prepare acrolein in each of the following ways:

1st: From glycerol according to the test given on page 179.

2nd: Oxidize one or two drops of allyl alcohol with potassium

bichromate and H_2SO_4, similar to the oxidation of ethyl alcohol in Exp. 84.

Exp. 87. To about 5 c.c. of an aqueous solution of chloral hydrate add a few cubic centimeters of strong NaOH solution and boil. Note odor of chloroform.

Exp. 88. Isobenzonitril test for chloral or chloroform: Place a few drops of a dilute chloral hydrate solution (or a small drop of chloroform) in a test-tube, add 5 c.c. of an alcoholic solution of alkali hydrate* (NaOH or KOH) and one drop only of fresh aniline oil. Heat till the mixture just begins to boil and note the odor of the nitril.

Exp. 89. Test 2 or 3 c.c. of an aqueous solution of aldehyde with an equal volume of Schiff's reagent.

Experiments with Acetone.

Exp. 90. Preparation of acetone: Heat a few grams of dried calcium acetate in an ignition tube, collect the distillate, which consists of an impure acetone. If this is mixed with a little water and filtered, part of the impurities may be removed, and the filtrate tested for acetone by the following experiment.

Exp. 91. Dilute the filtrate from the last experiment with distilled water; add a crystal of sodium nitroprusside. After the crystal is dissolved, add a few drops of acetic acid, and then an excess of ammonia water. A violet or purple color indicates the presence of acetone. Using a dilute solution of acetone in place of the alcohol in experiment 72, on page 383, produce iodoform crystals by similar reaction with iodine and sodium or potassium carbonate.

Exp. 92. Acetone may be dissolved or mixed with water in all proportions; but, upon saturating the water with KOH, the acetone will form a separate layer which may be drawn off as in the separation of alcohol in experiment 76, page 384.

* If alcoholic potash or soda is not at hand, the test may be performed with 5 c.c. of alcohol and 1 or 2 c.c. of a 40% aqueous solution of NaOH.

Experiments with Ethers.

Exp. 93.   Into a large test-tube put a little alcohol and about half its volume of strong H_2SO_4.   Warm gently and notice the odor.

Ether is formed by two reactions.   First, $C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O$.   Then the ethyl-hydrogen sulphate ($C_2H_5HSO_4$) is acted upon by a second molecule of H_2SO_4, as follows: $C_2H_5HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4$.

Exp. 94.   The production of compound ethers may be demonstrated by the test for acetic acid forming ethyl acetate, page 100, or by the following experiment used to detect butyric acid in gastric contents:

Exp. 95.   Mix in a test-tube 5 c.c. of a dilute ($1/2\%$) solution of butyric acid with an equal volume of strong H_2SO_4 and as much strong alcohol.   Heat gently and note the odor of ethylbutyrate (pineapples).

Exp. 96.   Mix carefully equal portions of cold alcohol and strong H_2SO_4, about 10 c.c. of each.   Then pour the mixture into about 200 c.c. of water and add in small portions barium carbonate in excess.   Allow to stand a little, filter and test filtrate for barium.   Concentrate the solution of barium ethyl sulphate thus obtained over a water bath to about half its volume.   Then mix about 10 c.c. with 2 or 3 c.c. of dilute HCl and distil.   Test a portion of the distillate for acid and for SO_4.   Warm the remainder with an equal volume of alcohol and note if ether is produced.

Exp. 97.   The action of fixed alkalies on compound ethers is known as "saponification."   It may be illustrated by heating 10 c.c. of ethyl acetate with 80 c.c. of a 10% NaOH solution for 30 to 40 minutes, when the odor of ethyl acetate should be destroyed.   The flask should be connected with a reflux condenser and the heat applied by immersing the flask in boiling water.   Write reaction.

Experiments with Organic Acids $(C_nH_{2n}O_2)$.

Exp. 98. Introduce into a small flask (250 c.c. capacity) about 30 c.c. of anhydrous glycerin and an equal weight of oxalic acid crystals. Boil for several minutes; CO_2 is given off and a compound formed between the acid and glycerin; then, upon addition of more acid and continued heating, formic acid may be distilled. Collect about 10 c.c. of distillate; test reaction with litmus-paper. Make silver-mirror test, described on page 386, Exp. 85. The silver solution will be reduced, but difficulty will be experienced in obtaining the mirror.

Exp. 99. To 5 c.c. of formic acid solution add 2 or 3 c.c. of dilute H_2SO_4 (1–5) and a little potassium permanganate solution; heat the mixture and conduct the gas evolved into a tube containing lime water.

Exp. 100. From a mixture of formic acid, alcohol, and sulphuric acid, ethyl formate may be evolved in a manner similar to that in the production of ethyl acetate (page 100). Compare the odors of these two ethers.

Exp. 101. To a dilute aqueous solution of acetone add potassium permanganate slowly until the mixture is permanently colored pink; filter, add dilute sulphuric acid and distil until 1 or 2 c.c. of distillate are obtained. This may be tested for acetic acid by litmus paper and ferric chloride.

Exp. 102. To a dilute solution of ferric chloride add a little acetic acid; divide the solution into two parts; to one add mercuric chloride and to the other HCl, and note results.

Exp. 103. Repeat Exp. 102, using diacetic acid in place of acetic.

Exp. 104. Repeat Exp. 102, using meconic acid* in place of acetic.

Compare results of these three experiments and save record for future use in the study of saliva.

* Laudanum diluted with water till color is light brown may be used.

Exp. 105. In a small flask saponify a little butter by heating with alcoholic potash over a steam bath till mixture is dry. Dissolve in water, add dilute H_2SO_4, and distil off a portion of the butyric acid. Record whatever can be learned from this experiment regarding the physical properties of the butyric acid.

Exp. 106. In separate test-tubes take about 5 c.c. of solutions of stearic and oleic acids in carbon tetrachloride. Add to each about 1 c.c. of a one-tenth per cent solution of iodine also in carbon tetrachloride, allow to stand for some time, and explain *fully* the difference in action exhibited by the two fatty acids.

Experiments with Organic Acids not of the $C_nH_{2n}O_2$ Series.

Exp. 107. To a dilute solution of permanganate of potassium add a few drops of sulphuric acid and heat nearly to boiling. Note if any change takes place. Now add a few crystals of oxalic acid and watch carefully. Explain the use of sulphuric acid.

Exp. 108. In separate test-tubes, insoluble oxalates may be produced by adding a solution of ammonium oxalate to a solution of (*a*) calcium chloride, (*b*) silver nitrate, (*c*) zinc sulphate, (*d*) copper sulphate, (*e*) lead nitrate.

Exp. 109. Place in an ignition tube, fitted with delivery tube to collect evolved gas in test-tube, about 3 grams of dry calcium oxalate. Heat strongly and test gas evolved with lighted match or splinter. After ignition tube has become *cold* add dilute H_2SO_4 and pass gas evolved into lime water.

Exp. 110. Dissolve about 3 grams of dry oxalic acid (100° C.) in a test-tube half full of methyl alcohol. It will probably be necessary to boil the mixture before solution is complete and great care must be used to avoid burning of the alcohol. The use of a water bath is recommended. As the hot mixture cools, dimethyloxalate will crystallize out.

Separate sufficient of the crystals to obtain melting-point, which should be about 54° C.

Exp. 111. The ester prepared in above experiment may be dissolved in alcohol and upon addition of NH_4OH will give a precipitate of oxamide.

Exp. 112. Take a test-tube half full of calcium chloride (10%), make strongly alkaline with NH_4OH and pass CO_2 into the mixture for several minutes. A solution of calcium carbonate will result.

Write reaction, $CaCl_2 + 2 CO_2 + 4 NH_4OH = ?$. Heat the solution of calcium carbonate just produced till a precipitate of $CaCO_3$ is produced.

Write reactions showing the formation of $CaH_2(CO_3)_2$ and the precipitation of $CaCO_3$ from the acid salt.

Exp. 113. To 1/3 test-tube of cider vinegar add a few cubic centimeters of basic acetate of lead solution; a bulky precipitate of lead malate separates.

Exp. 114. Dilute a few drops of neutral ferric chloride solution until no color is discernible, then to 10 c.c. of this dilution add 4 to 5 drops of 1/2% solution of lactic acid. A greenish-yellow color constitutes a positive test.

In practical application of this test, it needs further confirmation by boiling the unknown solution with a drop or two of HCl and then extracting with ether. Evaporate the ether, take up the residue in 2 or 3 c.c. of water and repeat the test as given above. If the yellow color persists, it is due to lactic acid.

Experiments with Cyanogen Compounds. (*Chap. XXV.*)

Exp. 115. In a large test-tube dissolve one half gram or *less* of potassium ferrocyanide in about 4 c.c. of water. Add a little H_2SO_4 and boil, conducting the gas evolved into a beaker condenser (Fig. 35) by means of a bent glass tube. Note the odor of this dilute solution. (Do not smell of the contents of generating tube, as the strong acid is intensely poisonous.) Write reaction.

Exp. 116.   To one half of the dilute hydrocyanic acid prepared in the previous experiment add a drop or two of $AgNO_3$ solution with a little HNO_3.   After the precipitate has settled, decant the fluid, then add an excess of ammonia water.

Exp. 117.   To the other half of the HCN from Exp. 115 add a little solution of ferrous sulphate; also a few drops of ferric chloride solution; then a little KOH solution; mix thoroughly and acidify with HCl.   A blue precipitate, $Fe_4(FeCy_6)_3$, is a test for HCN or any soluble cyanide.

Exp. 118.   To a few drops of KCN solution add a little yellow ammonium sulphide, $(NH_4)_2S$, and evaporate to dryness. Dissolve in water; acidify with HCl and add Fe_2Cl_6 solution.

Exp. 119.   In a small flask boil a solution of KCN.   While boiling, test the vapors for ammonia gas.   Solution of potassium formate remains in the flask.

Complete reaction, $KCN + 2 H_2O = ?$.

Exp. 120.   To a little dilute (2%) solution of $K_4Fe(CN)_6$ add a little bromine water and boil.   Prove the formation of $K_3Fe(CN)_6$ by use of $FeCl_3$.

From this experiment what is the relative valence of iron in the two compounds?   Why?

Exp. 121.   To a fresh solution of $K_3Fe(CN)_6$ add a little 10% KOH solution and some PbO, shake and filter.   To the clear filtrate add $FeCl_3$.

Give reason for the statement that the PbO has acted as a reducing agent.

Exp. 122.   Dissolve a piece of potassium ferricyanide, as large as a pea, in 5 c.c. water, add 2 c.c. of a solution of potassium ferrocyanide.   Dilute to a test-tube full with distilled water and put equal amounts of this solution into 2 shell tubes.   Examine the color through the length of tube, then add to one tube 2 or 3 drops of strong HCl.   Examine again and notice that a trace of prussian blue has been produced.   Explain.

Experiments with Amines and Amides. (*Chap. XXVI.*)

Exp. 123. Distil 60 c.c. of ammonium acetate in a glass retort, as in Fig. 35, fitted with a thermometer. Acetamide should distil at about 222° C. and condense as a white solid in the receiver.
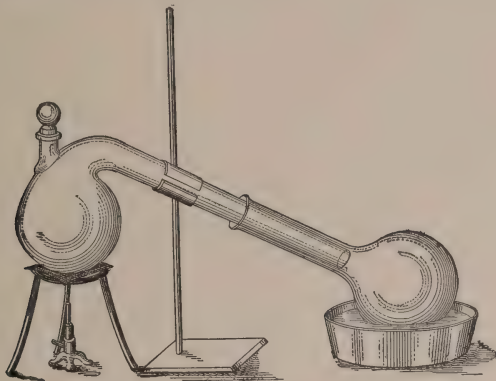
Fig. 35.

Exp. 124. In a 500-c.c. flask place 10 grams of strong, fresh, bleaching powder; add 3 grams of acetamide dissolved in about 10 c.c. of water. Mix as thoroughly as possible and add slowly 25 c.c. of a 20% solution of NaOH. Distil with steam, collecting distillate in 15 c.c. of cold water.

Exp. 125. To a little of the water solution of methyl amine prepared in the last experiment add 2 or 3 drops of chloroform and a little alcoholic potash. This mixture upon warming will give carbylamine. Note the odor. Warm a little of the solution with a little 5% NaOH. Test the vapor given off with litmus paper and compare with ordinary qualitative test for ammonia.

Urea and Uric Acid.

Exp. 126. Make separate solutions of 10 grams of potassium cyanate* and 8.25 grams of ammonium sulphate. Mix and

* For method of making potassium cyanate, see Preparation of Reagents and Organic Compounds, in the Appendix.

evaporate on a water bath in a shallow dish. Separate the potassium sulphate as the evaporation proceeds; finally, evaporate to dryness and extract with absolute alcohol. Evaporate alcohol and reserve the urea for subsequent experiments. (See Urea, page 237.)

Exp. 127. Heat a few crystals of urea in a test-tube until they fuse and no more gas is given off; cool, and dissolve the fused mass in water; add 1 or 2 c.c. of strong NaOH solution, then not more than 1 or 2 drops of a 1% $CuSO_4$ solution. Note the pink to violet color produced. This constitutes the biuret reaction used in physiological chemistry as a test for albumoses and peptones. Biuret is formed from urea as follows:

$$2\ O=C\big\langle{}^{NH_2}_{NH_2} = {O=C\big\langle{}^{NH_2}_{}\atop O=C\big\langle{}_{NH_2}^{}}\big\rangle NH + NH_3.$$
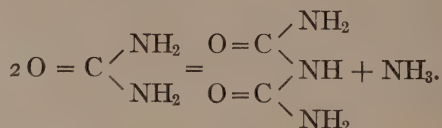
Exp. 128. Produce crystals of urea nitrate and oxalate (page 238) and examine under the microscope. *Repeat with* urea obtained from urine.

This experiment may be performed by concentrating to about 1/5 its bulk a little urine and using the concentrated solution as a solution of urea.

Exp. 129. Treat 5 c.c. of urea solution (urine may be used) with a little sodium hypochlorite or hypobromite; note results and study reaction given on page 238.

Exp. 130. Heat one-third of a test-tube of urine with barium hydroxide (baryta-water); test vapor with red litmus for NH_3.

Exp. 131. *Murexide test* for uric acid: Place a very small quantity of uric acid on a porcelain crucible cover, or in a small evaporating dish. Add 2 or 3 drops of strong nitric acid and evaporate to dryness over a water-bath. A yellowish-red residue remains, which changes to a purplish red upon addition of a drop of strong NH_4OH, and purple-violet upon further

addition of a drop of KOH solution, the color disappearing upon standing or upon the application of heat. (Difference from xanthin, which also gives a deeper red color.)

Exp. 132. Repeat No. 131, using caffein in place of uric acid.

Exp. 133. Heat a little sodium acid urate in a dilute solution of NaH_2PO_4. Allow to cool, and examine any deposit for uric acid crystals. Test reaction of solution both hot and cold (page 242).

Exp. 134. Mix, and allow to stand for some time at reduced temperature, 30 c.c. of urine (a 2% urea solution), 2 or 3 c.c. of strong Na_2CO_3 solution, and 5 c.c. of saturated NH_4Cl solution.

A precipitate consists of ammonium urate.

Examine under the microscope and make murexide test.

Experiments with Aromatic Hydrocarbons.

Exp. 135. Into a small and thoroughly dry flask (250 c.c.) introduce about 50 grams of a mixture consisting of 1 part of benzoic acid and 2 parts of quick-lime; connect with a beaker condenser (Fig. 36) and heat. Benzene (benzol) distils over:

$$CaO + C_6H_5COOH =$$
$$CaCO_3 + C_6H_6.$$

Exp. 136. Turn a little of the benzene prepared in the last experiment onto some water contained in a porcelain capsule. Set fire to it and note that it

FIG. 36.

burns with a *smoky* flame. Cool a few cubic centimeters of pure benzene contained in a narrow test-tube by immersion in a freezing mixture of ice and salt.

Exp. 137. In a wide test-tube mix 5 c.c. of concentrated H_2SO_4 with about half its volume of *strong* HNO_3; cool in ice-

water or cold running water, and add *very slowly* about 2 c.c. of benzene. Nitrobenzene is formed and may be separated as a heavy oily liquid by pouring the mixture into an excess of water. Notice the odor of oil of bitter almonds.

Exp. 138. Observing the same precaution against overheating as given in Exp. 137 reduce nitrobenzene to amino-benzene as follows: In a large test-tube or small flask place 1 or 2 c.c. of nitrobenzene with three times its weight of tin powder. To this add 10 or 15 c.c. of strong HCl in successive small portions, keeping cool as indicated. The odor of nitrobenzene should be replaced by that of aniline.

Exp. 139. Heat a mixture of 2 c.c. of aniline, 5 c.c. of water and 1 c.c. of strong sulphuric acid to the boiling point; then set aside where it may cool slowly. Crystals of aniline sulphate will separate.

Exp. 140. Repeat preceding experiment, using 5 c.c. of aniline, 5 c.c. of water and 10 c.c. of strong hydrochloric acid. When the mixture has become thoroughly cold filter off the crystals of aniline hydrochloride and dry in a current of air. Test solubility in water, using only a very little of the crystallized salt.

Exp. 141. Place 5 c.c. of an aqueous solution of aniline in each of three test-tubes. Add to the first a few drops of bromine water; to the second a few drops of dilute ferric chloride; and to the third a solution of hypochlorite of calcium or sodium.

Exp. 142. Shake together in a test-tube 1 part of aniline oil and 5 parts of water. Is the oil soluble in water?

Agitate with HCl added in small portions till liquid becomes clear. Explain.

Exp. 143. To a few cubic centimeters of a 3% phenol solution add dilute bromine water. A yellowish-white crystalline precipitate of tribromphenol is produced (see page 184).

Exp. 144. To an aqueous solution of phenol add a few drops of solution of ferric chloride.

Exp. 145. To 5 c.c. of an aqueous solution of phenol add

one quarter its volume of ammonia water and then a few drops of sodium hypochlorite solution. Mix and warm. A blue-green color develops which turns red upon addition of hydrochloric acid to slight acid reaction.

Exp. 146. Repeat Exps. 143 and 144, using an aqueous solution of cresol in place of phenol.

Exp. 147. To a test-tube 1/3 full of nitric acid (50% absolute HNO_3), add, 1 drop at a time, about 1 c.c. of phenol with constant agitation. When the phenol has all been added heat carefully to boiling. Allow to cool slowly when trinitrophenol will be precipitated.

Exp. 148. Evaporate a few drops of a 1% solution of potassium nitrate to dryness in a small porcelain capsule. Add 2 c.c. of phenoldisulphonic acid;* stir thoroughly, and keep hot for three to five minutes; dilute with water, make strongly alkaline with ammonia, and note the intense yellow color of ammonium picrate. The reaction is used as a test for nitrates in drinking water.

Exp. 149. Determine melting-point of benzoic acid.

Exp. 150. Arrange two watch glasses of equal size with the concave surfaces together and a piece of filter paper stretched between them. The glasses may be held together with a small brass clamp.

A little benzoic acid placed in the lower glass may be sublimed by means of a gentle heat through the paper and collected upon the upper glass. Examine the sublimate by polarized light. See Plate V, Fig. 5, opposite page 204.

Exp. 151. With an aqueous solution of benzaldehyde determine whether Tollen's test for aldehydes (Exp. 85) is applicable to aromatic compounds.

Exp. 152. Boil 10 c.c. of oil of wintergreen with a little of 20% NaOH; keep the volume constant by frequent addition of water. When the oil has entirely disappeared, cool and add HCl

* For method of preparation of phenoldisulphonic acid, see Appendix.

to acid reaction. Salicylic acid will separate, white and crystalline.

Exp. 153. To a dilute solution of sodium salicylate, or saturated aqueous solution of salicylic acid, add a few drops of Fe_2Cl_6. A slight amount of salicylates in the urine will produce this color when a test is being made for diacetic acid (q. v.).

Exp. 154. Mix in a large test-tube or small flask a little dry slaked lime and salicylic acid, connect with a beaker condenser (see cut on page 395) and distil. Test distillate for phenol. Write reaction.

Note. — After the first heating, the tube containing the lime and acid may be inclined so that any moisture in distillate will run into collecting tube rather than back onto the mixture.

EXPERIMENTS FOR PHYSIOLOGICAL CHEMISTRY.

Preparation of Oxidase.

Exp. 155. Clean thoroughly a small potato and grate the skin into a small beaker; cover with water and allow to stand in a cool place for an hour. Filter through coarse paper. Turn about 5 c.c. of the filtrate slowly into 25 c.c. of strong alcohol. The enzyme will be precipitated. Filter and test as follows:

Exp. 156. Transfer the moist precipitate from the above experiment into half a test-tube of distilled water. Shake frequently for about ten minutes and filter. The filtrate will contain oxidizing enzymes in solution. Divide the solution into two parts; to one add a few drops of tincture of guaiacum, and to the other a little of a 1% solution of pyrocatechol. The guaiacum gives a blue color, and the pyrocatechol a red-brown color in the presence of oxidizing enzymes.

Experiments with Enzymes.

Hydrolytic enzymes produce cleavage of the molecule.

Exp. 157. Take five test-tubes, *a–b–c–d–e*. Make a thin paste by rubbing one-sixth of a yeast cake with water, and place

a little in each of the five tubes; then fill *a* with a dilute glucose
solution; *b* with a dilute solution of milk sugar; *c* with dilute
solution of cane sugar; to *d* add
a little invertase (an enzyme from
the mucosa of the small intes-
tine of a pig) (see Appendix);
then fill with the same solution
used for *c*. Prepare *e* exactly
the same as *d* except that be-
fore adding the sugar solution
the enzymes are boiled for at least
one minute. Fit each tube with
short delivery tube and allow to
stand overnight.
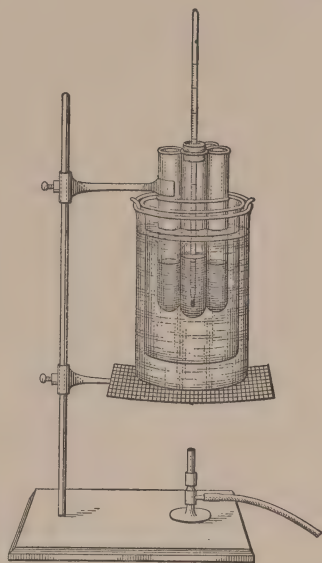
Fig. 37.

Exp. 158. Take four test-tubes,
a–*b*–*c*–*d*, arrange as indicated in
Fig. 37, and half fill each with some
thin starch paste (see page 430 of
Appendix). Into *a* put a little of
the yeast from last experiment;
into *b* a little pepsin solution; into
c a little saliva (the enzyme of the saliva in ptyalin); into *d* a
little invertase as used in preceding experiment. Warm all the
tubes to about 37 or 38° C., and allow to stand overnight; then
test contents of each tube for a reducing sugar which may have
been produced from the starch. (Use Exp. 167.)

Exp. 159. The student may prepare a fat-splitting enzyme
(lipase) from an animal source, pig's pancreas, according to
direction in the appendix; or from a vegetable source, castor
beans, as follows:

Fat Digestion with Lipase (Castor Bean). — Grind with the
powder,* in the order named, 5 c.c. N/10 sulphuric acid, 5 c.c. of
neutral cotton oil (sp. gr. 0.92) and 5 c.c. lukewarm water. The

* For preparation of powder, see page 428.

water should be added a little at a time and thoroughly worked
into the mixture so that at the end of the operation a good
emulsion is secured. Cover the evaporating dish and let stand
in a warm place overnight.

Add 50 c.c. of alcohol, 10 c.c. ether, and a few drops phenol-
phthalein and titrate with N/1 sodium hydrate. Calculate the
amount of fatty acid and the per cent of fat digestion.

Exp. 160. To one-third of a test-tube of milk, colored slightly
blue with nearly neutral litmus solution, add half as much
solution of lipase (fresh pancreatic extract) and keep at about
40° C. for twenty to thirty minutes. Sufficient fat acid should
be separated to change the blue litmus to red. Write reaction.

Exp. 161. Dialyse thoroughly some saliva, using three or
four changes of water, then see if the effect of dialysis on the
amylolytic ferment of the saliva is the same as on the amylolytic
ferment of the pancreatic juice, page 322.

Experiments with Sugars.

Exp. 162. Fill a test-tube about one third full of dry straw.
Cover with 10% hydrochloric acid; boil, collecting the distillate
in a dry tube. Divide the distillate into two parts, and make
the following tests for furfuraldehyde which has been produced
from the pentose contained in the straw. Treat the contents
of one tube with a little aniline and hydrochloric acid. Red
coloration indicates the presence of furfuraldehyde. To the
contents of the other tube add a little solution of casein (skimmed
milk) and underlay with strong sulphuric acid. Furfurol will
give a blue or purple line at the point of contact of the two liquids.

Monosaccharides. — Exp. 163. Test for C and H, using
cane-sugar. Make closed-tube test for H, which is given off as
H_2O, and for C, which remains as such in tube. (See page 105.)
Write reactions.

Exp. 164. *Molisch's Test for Carbohydrates.* — To a few
cubic centimeters of a 3% glucose solution add a few drops of

an alcoholic solution of α-naphthol, and carefully underlay the mixture with strong H_2SO_4.

Exp. 165. To a few cubic centimeters of $CuSO_4$ solution in a test-tube add a little NaOH. Boil and write reaction.

Exp. 166. Repeat Exp. 165 with the addition of Rochelle salt; if solution remains clear on boiling, add a few drops of a glucose solution.

Exp. 167. *Fehling's Test for Sugars.* — Take about 5 c.c. of Fehling's solution* made by mixing equal parts of the $CuSO_4$ solution and the alkaline tartrate on side shelf. Boil and add immediately a few drops of glucose solution. Set aside for a few minutes, watching the results.

Exp. 168. Repeat Exp. 167, using diabetic urine instead of glucose.

Exp. 169. Repeat Exp. 167 without heat and allow to stand for twenty-four hours.

Exp. 170. 5 c.c. of Benedict's solution (for prep. see Appendix). Add 8 or 10 drops of a 2% glucose solution. Heat the mixture to boiling; keep at this temperature for one or two minutes.

Exp. 171. *Barfoed's Test.* — To about 5 c.c. of Barfoed's reagent add a few drops of glucose solution; boil and set aside for a few minutes, watching results.

Exp. 172. *Fermentation Test.* — Fill the "fermentation tube" (Fig. 38) found in the desk

FIG. 38.

with glucose solution; add a little yeast; insert stopper, with long arm of tube extending into glucose mixture nearly to bottom of tube, and allow it to stand upright, in a *warm* place, overnight. On the next day, test the gas, with which the tube is filled, with lime water.

Exp. 173. *Phenylhydrazine Test.* — Place about 5 c.c. of

* For preparation, see Appendix.

glucose solution in a test-tube; add an equal volume of phenyl-
hydrazine solution; keep the tube in boiling water for thirty
minutes.   Allow to cool gradually.   Examine the precipitate
microscopically and sketch the crystals.

Disaccharides. — Exp. 174.   Use dilute solutions of cane-
sugar, milk-sugar, and maltose, and make on each Fehling's
test (Exp. 167), Barfoed's test (Exp. 171), and the phenylhy-
drazine test (Exp. 173).   Sketch the different osazone crystals
obtained.

Exp. 175.   To a dilute solution of cane-sugar add a few
drops of dilute H_2SO_4 and boil for five minutes.   Cool the
mixture and make slightly alkaline with NaOH.   With this solu-
tion perform Exps. 167, 171, and 173.   Explain results.   Com-
pare with Exp. 174.

Experiments with Starches and Cellulose.

Polysaccharides. — Exp. 176.   Examine potato, corn, and
wheat starch under the microscope, use a drop of water and
a cover glass.   Sketch the granules of each in notebook, and,
while still on the slide, treat with a dilute iodine solution.   Note
changes in appearance of granules.

Exp. 177.   Preparation of starch.   Grate a little raw potato.
Mix thoroughly with water and strain through "bolting" cloth
or stout coarse muslin.   After the liquid has run through, com-
press the cloth by twisting till no more liquid can be squeezed
out.   The starch has passed through the cloth and may be
washed by decantation, dried on filter paper, examined, and used
for the following experiments:

Exp. 178.   Make some starch paste by rubbing one gram of
starch to a smooth, *thin* paste with water; then slowly pour it
into 100 c.c. of boiling water, stirring constantly.   With this
solution compare a one per cent. solution of dextrine and a solu-
tion of glycogen * as follows:

* For the isolation of glycogen, see Appendix.

(*a*) Treat each by boiling with Fehling's solution.

(*b*) Add to 5 c.c. of each a few drops of tannic-acid solution.

(*c*) To each solution add a drop of iodine solution. Note color of mixture while cold. Heat nearly to boiling and allow to cool again, watching the color during process.

(*d*) To 5 c.c. of each solution add twice its volume of 66% alcohol.

(*e*) Tabulate results of the tests and formulate method of distinguishing these three substances from one another.

Experiments with Fats and Oils.

Exp. 179. Test solubility of olive oil in water, ether, chloroform, and alcohol, carefully avoiding the vicinity of a flame.

Exp. 180. Let one or two drops of an ether solution of the oil drop on a plain white paper, also an ether solution of a volatile oil found on side shelf. Watch behavior of the two oils, and report differences, if any.

Exp. 181. Dissolve a little butter in warm alcohol, examine with the microscope, and micropolariscope the crystals, which separate on cooling.

Note. — If possible perform the next experiment in triplicate, i.e., carry three experiments along at the same time using for "fat" the glyceryl ester of the three most common fat acids: Olein (lard oil or olive oil), Stearin (beef fat or tallow), Palmatin (bayberry wax or tallow, which contains a large amount of free palmitic acid).

Exp. 182. *Saponification.* — To about two grams of solid fat placed in a narrow beaker, or 150-c.c. Erlenmeyer flask, add 10 or 15 c.c. of alcoholic solution of potassium hydroxide. Allow the beaker to stand on the water bath till the alcohol is entirely evaporated, then dissolve the resulting soap in water; filter, if necessary, to obtain a clear solution and make the following tests:

(*a*) Add to a portion of solution a saturated solution of sodium chloride. What takes place?

(*b*) To another portion add a few cubic centimeters of a solution of calcium or magnesium chloride. Explain the results.

(*c*) Pour the remainder slowly, and with constant stirring, into warm dilute H_2SO_4, and heat on the water bath. What is the result? Write the equation. Transfer the mixture to a filter-paper which has been moistened with hot water, and wash with hot water till all H_2SO_4 is removed. Reserve the filtrates.

Exp. 183. *Fatty acids.*

(*a*) Dissolve a portion of the above precipitates (182 *c*) by warming with strong alcohol. Test the reaction of the solution. Examine the crystals, which separate upon standing, with microscope and micropolariscope. (Plate VII, Fig. 3, page 287.)

(*b*) Add to a portion a few cubic centimeters of a strong Na_2CO_3 solution, and heat till the fatty acids dissolve. Cool. What takes place? Explain the reaction. Reserve the jelly.

Exp. 184. Neutralize the filtrates of Exp. 182 *c* and evaporate almost to dryness on the water bath. Extract with alcohol and evaporate. Note the taste. Heat another portion of the residue with a little powdered dry $KHSO_4$ in a dry test-tube, and note the odor, which is due to acrolein, $CH_2 = CH - CHO$. Fuse some borax and glycerin on a platinum loop: green color.

Exp. 185. *Emulsification.* — (*a*) Put 1 to 2 c.c. of a solution of sodium carbonate (0.25%) on a watch glass, and place in the center a drop of rancid oil. The oil-drop soon shows a white rim, and a white milky opacity extends over the solution. Note with the microscope the active movements in the vicinity of the fat-drop, due to the separation of minute particles of oil (Gad's experiment).

(*b*) Take six test-tubes and arrange as follows:

    1. 10 c.c. of a 0.2% Na_2CO_3 solution + 2 drops of neutral oil.

    2. 10 c.c. of a 0.2% Na_2CO_3 solution + 2 drops of rancid oil.

3. 10 c.c. of soap-jelly (see 151 *b*), warm, + 2 drops of neutral oil.
4. 10 c.c. of albumin solution + 2 drops of neutral oil.
5. 10 c.c. of gum-arabic solution + 2 drops of neutral oil.
6. 10 c.c. of water + 2 drops of neutral oil.

Shake all the mixtures thoroughly and note the results. What conclusions do you form relative to the influence of conditions upon emulsification?

(*c*) Examine a drop of an emulsion under the microscope.

General Protein Reactions.

Exp. 186. Test dried egg-albumin for C, H, S, and N, according to the methods described on pages 194 and 195. Test casein for phosphorus, and dried blood for iron.

There are several reactions which are common to nearly all proteins. For the following tests use a solution of egg-albumin (1/50) in water, as a general type of a protein.

1. Color Reactions.

Exp. 187. *Xanthoproteic Test.* — To 10 c.c. of the albumin solution add one third as much concentrated HNO_3; there may or may not be a white precipitate produced (according to the nature of the protein and the concentration). Boil; the precipitate or liquid turns yellow. When the solution becomes cool add an excess of NH_4OH, which gives an orange color. (This color constitutes the essential part of the test.)

Exp. 188. *Millon's Test.* — Add a few drops of Millon's reagent* to a part of the albumin solution. A precipitate, which becomes brick-red upon heating, forms. The liquid is colored red in the presence of non-coagulable protein or minute traces of albumin.

---

* Mercuric nitrate in nitric acid. For the preparation of this and other reagents, see Appendix.

Exp. 189. *Piotrowski's Test.* — To a third portion add 2 drops of a *very* dilute solution of $CuSO_4$, and then 5 to 10 c.c. of a 40% solution of NaOH. The solution becomes blue or violet. Proteoses and peptones give a rose-red color (biuret reaction) if only a trace of copper sulphate is used; an excess of $CuSO_4$ gives a reddish-violet color, somewhat similar to that obtained in the presence of other proteins. This test responds with all proteins.

Exp. 190. Hopkins-Cole reaction: Mix 2 or 3 c.c. of the unknown protein solution with 3 or 4 c.c. of the reagent (gly-oxylic acid). Then carefully superimpose upon 5 c.c. of strong sulphuric acid in another test-tube.

The glyoxylic acid is made by the reduction of oxalic acid with nascent hydrogen produced by the action of sodium amal-gam and water. Formula is CHO.COOH.

2. *General Precipitants.*

Proteins are precipitated from solution by the following re-agents (peptones are exceptions in some cases):

Exp. 191. *Acetic Acid and Potassic Ferrocyanide.* — Make part of the solution to be tested strongly acid with acetic acid, and add a few drops of potassic ferrocyanide solution. A white flocculent precipitate is formed (not with peptones).

Exp. 192. *Alcohol.* — To another part add one or two vol-umes of alcohol.

Exp. 193. *Tannic Acid.* — Make the solution acid with acetic acid, and add a few drops of tannic-acid solution.

Exp. 194. *Potassio-mercuric Iodide.* — Make acid another portion with HCl, and add a few drops of the reagent.

Exp. 195. *Neutral Salts.* — Certain neutral salts precipitate most proteins. $(NH_4)_2SO_4$ added to complete saturation to protein solutions, faintly acid with acetic acid, precipitates all proteins, with the exception of peptones.

Experiments with Albumin and Globulin.

The albumins and globulins respond to all the general protein reactions.   Experiments 187 to 195.

Exp. 196.   A specimen of solid egg-albumin, prepared by evaporating a solution to dryness at 40° C., is provided.   Test its solubility in water, alcohol, acetic acid, KOH solution, and concentrated HCl.   Report results.

Perform the following additional experiments, using a dilute (1/50) solution of egg-albumin.

Exp. 197.   *Nitric-acid Test.* — Take 15 c.c. of the solution in a wine-glass, incline the glass, and allow 5 c.c. of concentrated HNO_3 to run slowly down the side to form an under layer. What other proteins respond to this test?

Exp. 198.   *Picric-acid Test.* — Take a portion of the albumin solution and add a few drops of a solution of picric acid acidified with citric acid (Esbach's reagent).   What other proteins respond to this test?

Exp. 199.   *Action of $(NH_4)_2SO_4$.* — To 10 c.c. of the albumin solution in a test-tube add some solid $(NH_4)_2SO_4$, shaking until solution is thoroughly saturated.   Allow to stand a little while, shaking occasionally, then filter, saving the filtrate to test for albumin by the heat test.   Report result.   Test the solubility of the precipitate on the filter-paper.

Exp. 200.   *Action of $MgSO_4$.* — Perform an experiment similar to Exp. 199 using solid $MgSO_4$ instead of $(NH_4)_2SO_4$. With what results?

Exp. 201.   *Salts of the Heavy Metals.* — Note the action of the following: $AgNO_3$, $HgCl_2$, $CuSO_4$, $Pb(C_2H_3O_2)_2$.   Use solutions of the salts and of albumin.

Why is white of egg an antidote in cases of metallic poisoning?

The following tests serve to distinguish the globulins from other proteins.

The tests may be made upon blood serum, or upon a globulin

(edestin) which may be separated from hemp seed according to preparation in Appendix, page 434.

Globulins.

Exp. 202. *Action of CO_2.* — To 5 c.c. of blood serum add 45 c.c. of ice-cold water. Place the mixture in a large test-tube or cylinder, surround it with ice-water, and pass through it a stream of CO_2. A flocculent precipitate (paraglobulin)* will be formed.

Exp. 203. *Precipitation by Dialysis.* — Into a parchment dialyzing tube, previously soaked in distilled water, pour 20 c.c. of serum, swing the tube, with its contents, into a large vessel of distilled water, which is to be changed at intervals. Let stand twenty-four hours, then examine the serum in the dialyzing tube; it will contain a flocculent precipitate of paraglobulin. Give explanation of cause of precipitation.

Exp. 204. Pour a solution of globulin, drop by drop, into a large volume of distilled water (in a beaker). What takes place? Explain.

Exp. 205. *Precipitation by Magnesium Sulphate.* — Saturate about 5 c.c. of globulin solution with solid magnesium sulphate. A heavy precipitate will be formed. Compare this with the action of the same salt on the egg-albumin solution. Paraglobulin is so completely precipitated by this salt that the method is used for its quantitative estimation.

Experiments with Keratin and Gelatin.

Keratins are characterized by their insolubility, and by their high content of loosely combined sulphur.

Exp. 206. Test solubility of keratin (nail or horn) in water, acids, alkalies, gastric and pancreatic juices.

Exp. 207. Warm a bit of keratin with 5 c.c. strong NaOH

---

* Paraglobulin is a name applied to the globulin separated from blood serum.

solution for a few minutes, and add a few drops of a lead acetate solution. What is the result?

Exp. 208. With a solution of gelatin make the usual tests for protein.

Exp. 209. Precipitate gelatin from dilute solution with the following reagents:

(*a*) Tannic acid.

(*b*) Alcohol.

(*c*) Acetic acid and potassium ferrocyanide.

(*d*) Mercuric chloride.

(*e*) Picric acid.

Experiments with Milk.

Exp. 210. Examine microscopically whole milk, skim-milk, and cream. Note the relative amounts of fat in the three varieties.

Exp. 211. Shake a little cream with chloroform in a test-tube; separate the chloroform, evaporate, and melt the fat residue obtained; allow it to cool slowly, when fat crystals will be obtained, which may be examined under the microscope and micropolariscope.

Exp. 212. With a lactometer take the specific gravity of whole milk and skim-milk and explain the difference in results.

Exp. 213. Test the reaction of milk with litmus.

Exp. 214. Dilute some milk with six or seven times its volume of water, and add acetic acid drop by drop till the casein is precipitated. Filter and reserve the precipitate. Test the filtrate for proteins, if any remain; determine if possible their character.

Exp. 215. Test another portion of the filtrate for carbohydrates, determining the variety present.

Exp. 216. To 50 c.c. of milk add a few drops of rennin solution; keep at a temperature of 40° C. for a few minutes, and explain results.

Exp. 217. Take a portion of the precipitated casein from Exp. 214, digest at 40° C. with pepsin HCl for twenty minutes or half an hour. While digesting, test other portions of casein, for solubility in water, in dilute acid and dilute alkali. Test also a portion for phosphorus by boiling in a test-tube with dilute nitric acid, cooling to at least 50° C., and adding ammonium molybdate solution.

Exp. 218. To a little skim-milk contained in a test-tube add a saturated solution of ammonium sulphate.

Experiments with Mucin.

Exp. 219. To a solution of mucin * found on the side shelf add acetic acid till precipitation takes place. Settle filter, wash, and test solubility in water, dilute alkali solution and 5% HCl.

Exp. 220. Make color-tests for proteins.

Exp. 221. Boil a little mucin solution with dilute HCl for several minutes. Cool, neutralize, and test for sugar.

Experiments with Protein Derivatives.

Exp. 222. *Preparation of Metaprotein.* — To a solution of egg-albumin add a few drops of a 0.5% solution of NaOH, and warm gently for a few minutes. With the solution thus obtained make the following tests:

Exp. 223. (*a*) *Effect of Heating.* — Boil some of the solution and report result.

(*b*) *Effect of Neutralizing.* — Add a drop of litmus solution, and cautiously neutralize.

Acid Metaprotein.

Exp. 224. Add a small quantity of a 0.2% HCl solution to a solution of egg-albumin, and warm at 40° C. for one half to one hour. Or cover with an excess of 0.2% HCl some meat cut

* For preparation of mucin solution from navel cord, see Appendix.

into fine pieces, and expose for a while to a temperature of 40° C. Filter. With either of the solutions thus obtained make same tests as on alkali metaprotein, and compare results. How distinguish between them?

Experiments with the Proteoses.

Albumoses (*Hemialbumose*). — This name includes four closely allied forms of albumose, namely: (1) Protoalbumose, (2) Deuteroalbumose; (3) Heteroalbumose; (4) Dysalbumose, an insoluble modification of heteroalbumose. Commercial peptone, which is substantially a mixture of albumoses and peptones, will be given out for use.

Exp. 225. Make a solution of the peptone in water, filter if necessary, and saturate with solid $(NH_4)_2SO_4$. Filter. The precipitate contains the albumoses, the filtrate the peptones. Reserve the filtrate for subsequent tests for peptone. Wash the precipitate with a saturated solution of ammonium sulphate; dissolve in water, and, with the solution obtained, perform the following tests, noting especially the tendency of albumose precipitates to dissolve upon the application of heat and to reappear upon cooling.

Using this solution of albumose, repeat Exps. 187, 188, 189, 197, 198. If no precipitate forms with HNO_3 in Exp. 197, add a drop or two of a saturated solution of common salt. (Deuteroalbumose gives this reaction only in the presence of HCl.)

Exp. 226. Saturate some of the solution with $(NH_4)_2SO_4$. Report the result.

Exp. 227. To some of the solution add two or three drops of acetic acid and then a saturated solution of NaCl. A precipitate forms, which dissolves on heating, and reappears on cooling.

Experiments with Peptones.

Exp. 228. Using the peptone solution prepared in manner above described from commercial peptone, repeat the experiments indicated in Exp. 225.

Exp. 229. *Effect of Heating.* — Boil some of the peptone solution. Report the result.

Exp. 230. *Power of Dialyzing.* — Dialyze some of the peptone solution. Use 10 c.c. of the peptone solution, and in the outside vessel about 100 c.c. of water, which in this case is not to be changed. After twenty-four hours test the outside water for peptone, employing the biuret test.

Exp. 231. *Action of Ammonium Sulphate.* — Saturate some of the peptone solution with solid $(NH_4)_2SO_4$. Report the result.

A number of unknown solutions will be given out to be tested for carbohydrates and proteins. A report of the results, together with the methods employed, is to be made.

Experiments on Blood.

Exp. 232. Test the reaction of blood with a piece of litmus-paper which has been previously soaked in a concentrated NaCl solution. To what is reaction due?

Exp. 233. *Blood-corpuscles.* — (*a*) Examine a drop of blood under the microscope. Sketch the red and white corpuscles.

(*b*) Note the difference between the corpuscles of mammals and those of birds and reptiles.

(*c*) Note the effect upon the red corpuscles produced by the addition of (1) water, (2) a concentrated solution of salt.

Exp. 234. *Hemoglobin Crystals.* — Place a drop of de-fibrinated rat's blood on a slide; add a drop or two of water; mix, and cover with a cover-glass. Sketch the crystals which separate after a few minutes. Or instead of above add a few drops of ether to some blood in a test-tube; shake thoroughly until the blood becomes "laky," and then place the tube on ice till crystals appear.

Exp. 235. A spectroscope will be found ready for use in the laboratory, and the absorption-bands given by oxyhemoglobin and hemoglobin will be demonstrated. The student may prepare solutions for examination as follows:

(a) *Oxyhemoglobin.* — Use dilute blood (one part of defibrinated blood in fifty parts of distilled water).

(b) *Hemoglobin* (reduced hemoglobin). — Add to blood a few drops of strong ammonium sulphide, or one or two drops of freshly prepared Stokes's reagent.* Note the change in color produced by the addition of the reducing agent. Shake with air and note the rapid change to oxyhemoglobin.

(c) *Hemochromogen.* — To a little of the hemochromogen, reduced with ammonium sulphide, add a few drops of concentrated NaCl, and note the spectrum of reduced hematin or hemochromogen.

(d) *Carbonmonoxide Hemoglobin.* — Pass a current of illuminating gas through a dilute oxyhemoglobin solution for a few minutes and filter. Note the change of color. Try the effect on the solution of (1) ammonium sulphide; (2) Stokes's reagent; (3) shaking with air. Note the stability of the compound.

Exp. 236. Take the specific gravity of blood by filling a test-tube one-half full of benzene; add one drop of blood, and then add chloroform, a drop at a time, with careful but thorough mixing, until the drop of blood floats at about the middle of the mixture, indicating that the gravity of the mixture and of the blood are the same. The specific gravity of the benzene and chloroform may be taken in any convenient way.

Exp. 237. Make the guaiacum test for blood on a sample of dried blood; also on potato scrapings. The method is as follows:

To a little *clear solution* of blood or material obtained from potato scrapings, add some fresh tincture of guaiacum; then add a few drops of an ethereal solution of hydrogen peroxide, shake the mixture and note the blue color obtained.

From these two tests what do you gather about the value of

* Stokes's reagent consists of two parts of ferrous sulphate and three parts of tartaric acid dissolved in water and ammonia added to distinct alkaline reaction. There should be no permanent precipitate.

the guaiacum test for blood, and what is probably the cause of
the coloration?

Exp. 238. *The Benzidine Reaction* consists in adding to a
few c.c. of a saturated Benzidine solution in glacial acetic acid or
alcohol acidified with acetic acid an equal volume of commercial
H_2O_2 and 1 c.c. of the suspected solution. If blood is present
a green or blue color will develop. It is better to make a blank
test to insure purity of reagents.

Exp. 239. *Hemin Crystals* (*Teichmann's Test*). — Place a
bit of powdered dried blood on a glass slide; add a minute
crystal of NaCl (fresh blood contains sufficient NaCl) and two
drops of *glacial* acetic acid. Cover with a cover-glass and warm
gently over a flame until bubbles appear. On cooling, dark-
brown rhombic crystals, often crossed, separate (chloride of
hematin). Similar crystals can be obtained by using an alka-
line iodide or bromide in place of NaCl.

Exp. 240. *Coagulation of Blood.* — Observe the phenomena
of coagulation as it takes place (*a*) in a test-tube; (*b*) in a drop
of blood examined under the microscope. Explain fully.

Exp. 241. *Proteins of Blood-plasma.* — (*a*) Serum-albumin.
(*b*) Serum-globulin. Using blood-serum, separate and identify
these two proteins.

(*c*) *Fibrinogen.* — Fibrinogen is a globulin found in blood-
plasma, lymph, etc., together with paraglobulin. Like para-
globulin it responds to all the general precipitants and tests, and
in addition gives the reactions with CO_2, dialysis, and $MgSO_4$.
It is distinguished from paraglobulin easily by two reactions, viz.,
its power to coagulate, i.e., to form fibrin when acted on by fibrin
ferment, and its temperature of heat coagulation, which will be
found to be from 56° to 60° C.

Exp. 242. *Fibrin.* — (*a*) Note its physical properties.
(*b*) Note action of 0.2% hydrochloric acid.
(*c*) Apply the protein color tests.

Experiments with Muscle.

Exp. 243. Place 25 grams of fresh, finely chopped muscle in a beaker with 75 c.c. of 5% solution of common salt, and allow to stand for about one hour, with frequent stirring. (In the meanwhile perform Exp. 244.) Then filter off the liquid and make the following tests with the filtrate.

(a) Test for proteins.

(b) Having found proteins, pour a little of the solution into a beaker of water. Result. Inference (myosin).

(c) Make a fractional heat coagulation in the following manner (upon the care with which the temperatures given are adhered to, depends the success of the separation): Warm to from 44° to 50° C., and keep at that temperature for a few minutes. The coagulum is myosin [synonyms: paramyosinogen (Halliburton), musculin (older authors)]. In solutions the myosin, which has the properties of a globulin, becomes insoluble after a time, because it changes to myosinfibrin. In heating the solution as above, a slight cloud may appear at from 30° to 40° C. This is due to coagulation of soluble myogenfibrin. Now filter off the coagulated myosin.

Heat filtrate to from 55° to 65° C. The coagulum is myogen (synonym: myosinogen). In spontaneous coagulation of its solutions it forms, first, soluble myogenfibrin, and, finally, insoluble myogenfibrin. Filter.

Heat to from 70° to 90° C. Coagulum is serum albumin from the blood within the muscle, and is not a constituent of the muscle plasma. Filter.

Test filtrate for proteins. If it shows a slight biuret test, this is due either to incomplete precipitation by coagulation or to the post-mortem formation of albumose or peptone by auto-digestion (autolysis).

Exp. 244. Make an aqueous extract of muscle, and test for lactic acid by acidulating with H_2SO_4, extracting with ether,

and testing the ethereal extract with *very* dilute ferric chloride solution. The presence of lactic acid is shown by a bright-yellow color.

Experiments with Saliva.

Exp. 245. *Action of Saliva upon Starch.* — Take some filtered saliva in a test-tube and place in the water-bath at 40° C., for five or ten minutes. Put some starch paste into a second test-tube and place this also in the water-bath for a while, then mix the two (10 c.c. of starch paste to 3 c.c. of undiluted saliva) and return to the water bath. The starch is changed first to soluble starch (if originally a thick paste, it becomes fluid and loses its opalescence), then to erythrodextrin, which gives a red color with iodine, and finally to achroodextrin, which gives no reaction with iodine, and to maltose. Prove these changes as follows: Every minute or two take out a drop of the mixture, place it on a porcelain plate, and add a drop of iodine solution. This gives first a blue color, showing the presence of starch; later a violet color, due to the mixture of the blue of the starch reaction with the red caused by the dextrin; next a reddish-brown color, due to erythrodextrin alone (starch being absent), and finally no reaction at all with iodine, proving the absence of starch and erythrodextrin. The fluid now contains achroodextrin and maltose. Test for the latter with Fehling's solution and with Barfoed's reagent.

Exp. 246. *Influence of Conditions on Ptyalin and its Amylolytic Action.* — Report and explain the results of the following experiments:

(*a*) Boil a few cubic centimeters of the saliva, then add some starch paste, and place in the water bath at 40° C. After five minutes test for sugar.

(*b*) Take two test-tubes: put some starch paste in one, and saliva in the other, and cool them to 0° C., in a freezing mixture. Mix the two solutions, and keep the mixture surrounded by

ice for several minutes, then test a portion for sugar. Now place the remainder in the water bath at 40° C., and after a time test for sugar.

(*c*) Carefully neutralize 20 c.c. of saliva with very dilute HCl (the 0.2% diluted), and dilute the whole to 100 c.c. Test the action of this neutralized saliva on starch.

(*d*) To 5 c.c. of starch paste add 10 c.c. of 0.2% HCl and 5 c.c. of neutral saliva, and expose the mixture for a while at 40° C., and test for sugar.

(*e*) To 5 c.c. of starch paste add 10 c.c. of a 0.5% solution of Na_2CO_3 and 5 c.c. of neutral saliva, and expose the mixture for a while at 40° C., and test for sugar.

(*f*) Carefully neutralize (*d*) and (*e*), and again test the action of the two on starch.

(*g*) Mix a little uncooked starch with saliva, expose to a temperature of 40° C. for a while, and test for sugar.

Exp. 247. In three separate test-tubes place a few cubic centimeters of dilute solutions of KCNS or NH_4CNS, of meconic acid, and of acetic acid; add to each a few drops of ferric chloride, and notice that a similar color is obtained in each case. Divide the contents of each tube into two portions, and to one set add HCl; to the other add mercuric-chloride solution. Formulate a method of distinguishing from the sulphocyanates, meconates, and acetates.

Analysis of Gastric Contents and Experiments with Pepsin.

The following solutions will be found in the laboratory:

A. *A 0.2% Solution of HCl.* — This is prepared by diluting 6.5 c.c. of concentrated HCl (sp. gr. 1.19) with distilled water to 1 liter.

B. *A Solution of Pepsin.* — Prepared by dissolving two grams of pepsin in 1000 c.c. of water.

C. *A Pepsin-hydrochloric-acid Solution.* — Prepared by dissolving two grams of pepsin in 1000 c.c. of solution A.

Or, add to 150 c.c. of solution A about 10 c.c. of the glycerol extract of the mucous membrane of the stomach.

Exp. 248.   Take five test-tubes and label *a*, *b*, *c*, *d*, *e*.   Fill as indicated below.   Place in a water bath at 40° C., and examine an hour later, and again the next day.

(*a*) 3 c.c. pepsin solution + 10 c.c. water + a few shreds of fibrin.

(*b*) 10 c.c. 0.2% HCl + a few shreds of fibrin.

(*c*) 3 c.c. pepsin solution + 10 c.c. 0.2% HCl, and a few shreds of fibrin.

(*d*) 3 c.c. pepsin solution + 10 c.c. 0.2% HCl, boil, and then add a few shreds of fibrin.

(*e*) 3 c.c. pepsin solution + 10 c.c. 0.2% HCl, and a few shreds of fibrin which have been tied firmly together into a ball with a thread.

Make a note of all changes.

Exp. 249.   Filter *c*.   Neutralize with dilute Na_2CO_3.   Filter again.   Why?   Test the filtrate for the biuret reaction.

Exp. 250.   To 5 grams fibrin add 30 c.c. of the pepsin solution and 100 c.c. 0.2% HCl.   Set in the water bath at 40° C., stirring frequently, and leave in the water bath overnight. Observe the undigested residue, on the following day, and also a slight flocculent precipitate.   What is this precipitate?

Filter and carefully neutralize the filtrate.   A precipitate varying with the progress of the digestion will form.   What is it?

Remove this by filtration, and saturate this filtrate with $(NH_4)_2SO_4$.   Filter.   Save precipitate and filtrate.   Of what does each consist?

Exp. 251.   Dissolve the last precipitate of Exp. 250 in water, and try the following tests:

(*a*) Biuret reaction.

(*b*) Effect of boiling.

(*c*) Test with NHO_3, as in performing test for albumin in the urine, page 344.

Exp. 252. To the last filtrate of Exp. 250 add an equal volume of 95% alcohol, and stir thoroughly. The peptones will collect in a gummy mass about the stirring-rod.

(*a*) Determine the solubility of peptones in water.

(*b*) What is the effect of heat when so dissolved?

(*c*) Try the biuret reaction.

Exp. 253. *Demonstration of Rennet Enzyme.* — Place 10 c.c. of milk in each of three test-tubes. Label the test-tubes 1, 2, 3.

To 1 add a drop of neutralized glycerol extract of the mucous membrane of the stomach (made from the stomach of the calf).

To 2 add a drop of neutralized glycerol extract, and boil at once.

To 3 add a few cubic centimeters of $(NH_4)_2C_2O_4$ solution, and then a drop of a glycerol extract.

Place these tubes in the water bath at 40° C., and examine after five to ten minutes. Explain results in each case.

Continue heating tube 3 for half an hour, then add 2 or 3 drops $CaCl_4$ solution. The liquid instantly solidifies. Why?

Exp. 254. *Digestion of Casein.* — Determine the products of the digestion of the curd from the last experiment.

Exp. 255. *Tests for Free Hydrochloric Acid.* — Try each of the following tests with (*a*) HCl (0.2%, 0.05%, and 0.01% successively); (*b*) lactic acid (1%); (*c*) mixtures containing equal volumes of (*a*) and (*b*). Tabulate the results.

(*a*) *Dimethylaminoazobenzene.* — Use one or two drops of a 0.5% alcoholic solution. In the presence of free mineral acids a carmine-red color is obtained.

(*b*) *Gunzburg's Reagent.* — Phloroglucin, 2 grams; vanillin, 1 gram; alcohol, 100 c.c. Place two or three drops of the solution to be tested in a porcelain dish, add one or two drops of the reagent, and evaporate on a water bath. In the presence of free hydrochloric acid a rose-red color develops.

(*c*) *Boas' Reagent.* — This is prepared by dissolving 5 grams of resublimed resorcinol and a gram of cane-sugar in 100 grams

of 94% alcohol. Take three or four drops each of the reagent and the solution to be tested, and cautiously evaporate to dryness. In the presence of a free mineral acid a rose or vermillion red color is obtained. This gradually fades on cooling.

(d) *Tropæolin OO*. — Use one or two drops of a saturated alcoholic solution.

(e) *Congo-red*. — Use filter-paper which has been dipped into a solution of the reagent and then dried.

Exp. 256. To 5 c.c. egg-albumin in solution add 1 c.c. of 0.2% HCl. Mix thoroughly, and test for the presence of free HCl. What is the result? How do you explain it? Repeat the test, using a solution of peptone in place of the egg-albumin.

Exp. 257. *Tests for Lactic Acid*. — Uffelmann's reagent. Mix 10 c.c. of a 4% solution of carbolic acid with 20 c.c. of water, and add a drop or two of ferric chloride.

To 5 c.c. of the reagent add a few drops of the lactic-acid solution. Note the canary-yellow color.

Does the presence of free HCl interfere with this reaction?

A more delicate reagent is obtained by adding three or four drops of a 10% ferric-chloride solution to 50 c.c. of water. Such a solution has a *very faint* yellow color, which is distinctly intensified by lactic acid.

Using 5 c.c. of this nearly colorless solution for each experiment, note the effect of (a) 0.2% HCl; (b) acid phosphate of sodium; (c) alcohol; (d) glucose; (e) cane-sugar. What conclusions do you reach concerning the value of this test, when applied directly to the gastric contents?

The test is best applied to an aqueous solution of the ethereal extract of the gastric contents. Add to the contents two drops of HCl, boil to a syrup, and extract with ether. Dissolve the residue obtained upon evaporation of the ether in a little water, and test for lactic acid.

Exp. 258. Test for butyric acid; see ethyl butyrate, page 215.

Exp. 259. Test for acetic acid; see acetates (page 100).

Exp. 260. The acidity of the gastric contents may be determined as follows: To 5 c.c. of the filtered contents, diluted with 25 to 30 c.c. of water in an Erlenmeyer flask, add 2 or 3 drops of a solution of dimethylaminoazobenzene. Titrate with $N/10$ alkali till the color changes to a yellow which fairly matches the indicator; this represents the free HCl. To this mixture add a few drops of phenolphthalein solution, and continue the titration until a permanent pink color is obtained. The $N/10$ alkali used will represent the total acidity, combined HCl, and organic acids. The organic acids will not be present in gastric contents in the presence of any appreciable amount of free HCl, as they are derived almost entirely from fermentations which are inhibited by the hydrochloric acid.

Experiments with Pancreatic Juice.

Exp. 261. *Proteolytic Action.* — To 25 c.c. of a 1% solution of Na_2CO_3 add a few drops of the pancreatic extract. Place some pieces of fibrin in this liquid, and keep in the water bath at 40° C. till the fibrin has disappeared (one or two hours probably). Observe the digestion from time to time. Note that the fibrin does not swell and dissolve as in gastric digestion, but that it is eaten away from the edges.

Filter. What is the precipitate? Carefully neutralize the filtrate with 0.2% HCl. Another precipitate may appear. What is this?

Again filter, if necessary, and test the filtrate for proteoses and peptones as directed under gastric digestion.

Exp. 262. *Amylolytic Action.* — To some starch paste in a test-tube add a drop or two of the pancreatic extract and place in the water bath at 40° C. After a few minutes test for sugar and report the result.

Exp. 263. *The Piolytic (Fat-splitting) Action.* — For the demonstration of this action use natural pancreatic juice, or finely divided fresh pancreas, or a *recently prepared* extract.

To some perfectly neutral olive oil, colored faintly blue with litmus, add half its volume of the pancreatic extract, shake thoroughly, and keep at 40° C. for twenty minutes. Record the result. Reserve for next experiment.

Exp. 264. *Emulsifying Action.* — To 10 c.c. of a 0.2% solution of Na_2CO_3 add a few drops of the mixture used in Exp. 263. Shake thoroughly, and report the result. Referring to the earlier experiments on emulsification (see Fats), explain the efficacy of the pancreatic juice in emulsifying fats.

Experiments with Bile.

Exp. 265. *Color.* — Note the difference in color between human bile and ox bile. Explain.

Exp. 266. *Reaction.* — Dilute some bile with four parts of water. Immerse a strip of red litmus paper, then remove and wash with water. Note the reaction.

Exp. 267. *Nucleo-albumin.* — Dilute bile with twice its volume of water, filter if necessary, and add acetic acid. What is the precipitate? How distinguished from mucin?

Exp. 268. Filter 267 and test the filtrate for proteins. Report the result.

Exp. 269. *Separation of Bile Salts.* — Mix 20 c.c. of bile with animal charcoal to form a thick paste, and evaporate on the water bath to complete dryness. Pulverize the residue in a mortar, transfer to a flask, add 25 c.c. of absolute alcohol, and heat on the water bath for half an hour. Filter. To the filtrate add ether till a permanent precipitate forms. Let the mixture stand for a day or two, and then filter off the crystalline deposit of bile salts. Save the filtrate which contains cholesterin. (Plate VII, Fig. 4, page 287.)

Exp. 270. *Bile-pigments.* — (*a*) *Gmelin's Test.* — Take some bile in a wine-glass and underlay with *yellow* HNO_3, in the manner described in testing saliva for albumin. Notice the play of colors, beginning with green and passing through blue,

violet, and red to yellow, at the junction of the two liquids. Explain.

(*b*) *Iodine Test.* — Place 10 c.c. of dilute bile in a test-tube, and add slowly two or three cubic centimeters of dilute tincture of iodine, so that it forms an upper layer. A bright green ring forms at the line of contact.

Exp. 271. *Cholesterol.* — Examine under the microscope the crystals obtained by the cautious evaporation of the alcohol-ether filtrate of Exp. 269.

Concentrated H_2SO_4, containing a little iodine, gives with cholesterol a series of colors passing from violet to blue, then to green and finally red.

Exp. 272. *Action of Bile in Digestion.* — (*a*) Take three test-tubes. In one mix 10 c.c. of bile and 2 c.c. of neutral olive oil; in the second, 10 c.c. of bile and 2 c.c. of rancid olive oil; in the third, 10 c.c. of water and 2 c.c. of neutral oil. Shake and place in a water bath at 40° C. for some time. Note the extent and the permanency of the emulsion in each case.

(*b*) Into each of two funnels fit a filter-paper. Moisten one with water and the other with bile, and into each pour an equal volume of olive oil. Set aside for twelve hours (with a beaker under each funnel). Do you notice any difference in the rate of filtration?

(*c*) Add drop by drop a solution of bile salts to (*a*) a solution of egg-albumin; (*b*) a solution of acid-albumin; (*c*) a solution obtained by digesting a bit of fibrin in gastric juice and filtering. Explain the results.

APPENDIX.

REAGENTS.

It is desirable that all reagents be made with reference to the molecular weights of the substances employed. These may be from one to ten times the molecular weight per liter, while the solutions for practice are from one-tenth to one-fourth the molecular weight per liter. Salt solutions used as reagents are conveniently from five to ten per cent.; that is, a molar concentration is selected bringing the strength within these limits.

In the following list a few exceptions will be noted.

Ammonia (dilute). — Strong ammonia one part, distilled water two parts.

Ammonium Carbonate, 2M; 157 grams of commercial ammonium carbonate are dissolved by the aid of heat in about 900 c.c. water. After this has become cold add 75 c.c. of concentrated ammonium hydroxide, and make up volume to one liter.

Ammonium Chloride, 4M, or about a twenty per cent. solution.

Ammoniacal Cuprous Chloride may be made by dissolving copper oxide with metallic copper in dilute hydrochloric acid with the aid of heat. To the clear, cool, resulting solution add ammonia to marked alkaline reaction.

Ammonium Molybdate Solution for Phosphates. — This may be made by dissolving twenty grams of ammonium molybdate in a mixture of 250 c.c. NH_4OH and 250 c.c. of water. Then this solution is added to 1000 c.c. of nitric acid making 1500 c.c. of reagent. In using this solution as a test for phosphates it is necessary to heat the mixture to about 60° C.

If the reagent is prepared as follows it reacts without heating, is more sensitive than that produced by the first formula and is recommended as the better of the two. Dissolve 100 grams of molybdenum trioxide (molybdic acid) in 400 c.c. of dilute NH_4OH (10%). Allow to cool and add all at once 1000 c.c. of dilute HNO_3(HNO_3 three parts, H_2O two parts). The precipitate first formed is immediately redissolved and the product should be a perfectly clear, nearly colorless solution.

Ammonium oxalate, M/4, 35.52 grams per liter.

Ammoniacal Silver Solution. — Dissolve 10 grams of silver nitrate in 200 c.c. of water and add about 50 c.c. of strong ammonia, or an amount considerably in excess of that required to dissolve the precipitate first formed.

Ammonium Sulphide. — Saturate 300 c.c. of strong ammonia with hydrogen sulphide gas. Then add an equal volume of strong ammonia and sufficient water to make 1000 c.c. In this solution dissolve one or two grams of sulphur, giving the yellow or ammonium sulphide (polysulphide).

Barium Chloride, $BaCl_2.2 H_2O$, $M/2$, or 122.16 grams per liter.

Barfoed's Reagent. — Dissolve one part of copper acetate in fifteen parts of water; to each 200 c.c. of this solution add 5 c.c. of acetic acid containing thirty-eight per cent. of glacial acetic acid.

Benedict's Solution has the following composition:

	Gm. or c.c.
Copper sulphate (pure crystallized)............	17.3
Sodium or potassium citrate.................	173.0
Sodium carbonate (crystallized)...............	200.0
or one-half the weight of the anhydrous salt	
Distilled water to make......................	1000.0

The citrate and carbonate are dissolved together (with the aid of heat) in about 700 c.c. of water. The mixture is then poured (through a filter if necessary) into a larger beaker or casserole. The copper sulphate (which should be dissolved separately in

about 100 c.c. of water) is then poured slowly into the first solution with constant stirring. The mixture is then cooled and diluted to one liter.*

Benzidine Solution. — Saturated solution of benzidine in glacial acetic acid with an equal volume of peroxide of hydrogen solution. The two solutions are to be mixed when used as a test for blood.

The following method of making the benzidine solution is suggested by Hawk's Physiological Chemistry: 4.33 c.c. of glacial acetic acid is warmed in a small Erlenmeyer flask to about 50° C., a half gram of benzidine added, and the mixture heated eight or ten minutes at 50° C. and then the solution diluted with 19 c.c. of distilled water. If kept in a dark place it is fairly permanent.

Congo Red. — Two per cent. aqueous solution.

CuSO₄ Solution. — One per cent. for Biuret test.

Dimethyl-amino-azobenzene.—0.5 per cent. alcoholic solution.

Esbach's Reagent. — Picric acid ten grams, and citric acid 20 grams dissolved in sufficient water to make one liter of solution.

Fehling's Solution. — The Fehling's solution recommended for experiments in this book is one-half the strength frequently employed, and is prepared in separate solutions as follows: Dissolve 34.639 grams of pure crystallized copper sulphate in water, and make solution up to one liter. This constitutes the first part of the reagent. The second part may be made by dissolving 173 grams of Rochelle salts and 52.7 grams of caustic soda (NaOH) in water and making up to one liter. When prepared in this way 10 c.c. of each of these solutions mixed together will be reduced by 0.05 gram of glucose.

Ferric Chloride. — 2.5 per cent. solution acidified with HCl.

Goulard's Extract is a solution of lead subacetate, *q.v.*

Gram's Solution. — See iodine solution.

Gunzburg's Reagent. — Phloroglucin, 2 grams; vanillin, 1 gram; alcohol, 100 c.c.

* Jour. Amer. Med. Assoc., Oct. 7, 1911, p. 1193.

Hopkins-Cole Reagent, glyoxylic acid, $CHO.COOH.H_2O$, is prepared by saturating a liter of water with oxalic acid, adding sixty grams of sodium amalgam and allowing to stand until reduction is complete or until hydrogen ceases to be evolved. For use this solution should be filtered and diluted with two or three volumes of water.

Hydrochloric Acid (dilute). — Hydrochloric acid, strong, (sp. gr. 1.20) one part; distilled water, two parts.

Hypobromite Solution for Urea. — Consists of a mixture of equal parts of the following solutions kept separately and mixed for use:

Bromine Solution for Urea. — 125 grams KBr and 125 grams Br to one liter water.

NaOH Solution for Urea. — A 40 per cent. solution, or a ten molar solution.

Iodine Solution. — 10 grams iodine, 20 grams KI, made up with water to one liter.

Iodine Tincture. — See tincture.

Invertase. — Mix 500 gms. of " beer yeast," 200 c.c. of water and 10 gms. of sugar, allow to stand one hour. Add 50 c.c. of 60% alcohol and a little thymol. Filter, press or allow to dry, put the nearly dry mass in a flask, add twenty gms. of sugar and shake till solution is effected. Keep in ice chest.

If "beer yeast" is not available a solution of invertase, rather less satisfactory than the above, can be made as follows: Take one dozen compressed yeast cakes, grind with sand and mix with 500 c.c. of water, and a little chloroform as preservative. Allow to stand twelve hours and filter.

Iodine Solution. —

Lugol's solution is iodine five grams, potassium iodide ten grams, and sufficient distilled water to make one hundred grams. (U. S. P.)

Gram's solution: Iodine one gram, potassium iodide two grams, and sufficient distilled water to make two hundred grams.

Lead Subacetate, or basic acetate of lead. The U. S. P. method of preparation is as follows: lead acetate 180 grams, lead oxide 110 grams, distilled water to make 1000 grams. Rub lead oxide to a paste with 100 c.c. of water, dissolve lead acetate in 700 c.c. of boiling distilled water; add slowly with constant stirring to lead oxide and boil the mixture for half an hour. Cool and filter and make up to 1000 c.c. with water free from carbon dioxide.

Leucin. — See under Cystin, page 432.

Lipase. — From castor bean (see page 399). Remove the shells from ten grams of fresh beans, break them up as fine as possible and allow to stand overnight in a loosely stoppered test-tube full of alcohol ether mixture. Pour off; grind the beans to a powder in a small mortar, transfer to a test-tube and let stand under ether overnight. Filter with suction and wash two or three times with small amounts of the alcohol ether mixture.

Lipase. — From pancreas. Take a pig's pancreas, remove all fat, grind and allow to stand overnight. Then add four times its weight of 25% alcohol and allow to stand three days. Syphon off clear fluid and neutralize with sodium carbonate. The solution will contain a fat-splitting enzyme.

Lugol's Solution. — See Iodine.

Magnesia Mixture. — 125 grams of ammonium chloride, 125 grams of magnesium sulphate, dissolved in sufficient water to make one liter of solution, then add 125 c.c. of strong ammonia water.

Marmé's Reagent. — 10 grams potassium iodide, 5 grams cadmium iodide, 100 c.c. water.

Mercuric Chloride Solution. — Five per cent. $HgCl_2$ in distilled water.

Millon's Reagent. — To one part of mercury add two parts nitric acid of specific gravity 1.4, and heat on the water bath till the mercury is dissolved. Dilute with two volumes of water. Let the precipitate settle, and decant the clear fluid.

Molisch's Reagent for Carbohydrates. — Fifteen per cent. solution of α-naphthol in alcohol.

Nessler's Solution. — An alkaline solution of potassio-mercuric iodide, made as follows: Dissolve 35 grams of potassium iodide in about 200 c.c. of water. Dissolve 17 grams of mercuric chloride in 300 c.c. of hot water. Add the potassium iodide to the mercuric chloride, until the precipitate at first formed is nearly all redissolved. If the precipitate should entirely dissolve, add a few cubic centimeters of a saturated solution of mercuric chloride, until a slight permanent precipitate is obtained. After the mixture is cold, make up to one liter with a twenty per cent. solution of caustic potash. Allow to settle and use the clear solution.

Nitric Acid (dilute). — Strong HNO_3 (sp. gr., 1.42) one part, and water three parts.

Pancreatic Extract. — Obtain a fresh pancreas and soak in four times its weight of 25% alcohol for two or three days. Filter and make the solution neutral or very slightly alkaline with sodium carbonate. This solution will contain the fat-splitting enzyme.

Phenoldisulphonic Acid. — Phenoldisulphonic acid, for estimation of nitrates in water analysis, may be prepared by heating on a water bath for several hours a mixture of 555 grams of concentrated sulphuric acid and 45 grams of pure carbolic-acid crystals.

Phenyl-hydrazine Solution. — One gram phenyl-hydrazine hydrochloride and two grams sodium acetate dissolved in 10 c.c. water.

Picric-acid Solution (Esbach's Reagent). — Picric acid, ten grams; citric acid, twenty grams; dissolved in sufficient water to make one liter.

Potassium Ferrocyanide Solution. — $K_4Fe(CN)_6$, one-fourth molar solution (9.2%).

Schiff's Reagent. — Into 50 c.c. of a 2 per cent. solution of

Fuchsine or Rosaniline pass SO_2 gas until the solution is colorless. Then dilute with an equal volume of water and keep in small full bottles in a dark place.

Silver-nitrate Solution. — Drop solution, 1 : 8, used as a qualitative test for chlorine in urine.

Quantitative Solution for Chlorine Titration in Urine. — 29.075 grams silver nitrate, made up to one liter with water. 1 c.c. of this solution corresponds to 0.01 gram sodium chloride or 0.00607 gram chlorine, or a N/10 silver nitrate solution may be used, one c.c. of which will be equivalent to 0.00355 gram of chlorine.

Starch Paste (thin). — Rub about one-half gram of starch to a thin paste with cold water. Add sufficient boiling water to dissolve, then dilute to 100 or 150 c.c.

Sulphuric Acid (dilute). — Twenty per cent. strong H_2SO_4 in distilled water.

Tincture Iodine for Bile Test. — Dilute the U. S. P. tincture with alcohol until just transparent in test-tube.

Tollen's Reagent. — Make a 10 per cent. solution of $AgNO_3$ in dilute ammonia and just before using mix an equal volume of this solution with a 10% solution of NaOH.

Tropæolin oo. — Saturated alcoholic solution.

Uffelmann's Reagent. — Mix 10 c.c. of a four per cent. solution of carbolic acid with 20 c.c. of water, and add a drop or two of ferric chloride.

PREPARATIONS.

Creatin may be most conveniently prepared from a strong solution of Liebig's extract. Dissolve the extract in twenty parts of water, add basic lead acetate drop by drop to avoid more than a slight excess, then remove excess of lead; concentrate to a syrup over a water bath and allow to stand in a cool place, when creatin crystals will separate out. Two or three days' time may be required before the crystals are obtained. They may be washed with 88% alcohol and purified by recrystalliza-

tion from water. Hypoxanthin and sarcolactic acid may be obtained from the mother liquor.*

Creatinin may be prepared from creatin by boiling for ten or fifteen minutes with very dilute sulphuric acid. Neutralize the acid with $BaCO_3$, filter, evaporate to dryness on a water bath, and extract the creatinin with alcohol. Upon evaporation the creatinin is obtained in the form of crystals.

Cystin. — 1. Clean 200 grams of hair by washing with dilute HCl and then with ether. Boil the clean hair with 600 c.c. of concentrated HCl (specific gravity, 1.19) for four hours (in a three-liter flask with condenser) on a sand-bath in hood. Then let cool.

2. Add concentrated NaOH solution (750 c.c. H_2O, 500 grams NaOH) till the reaction is only faintly acid.

3. Add to the solution, which has begun to boil on neutralization, plenty of animal charcoal, and boil three-quarters of an hour.

4. Filter hot, being careful to moisten filter and funnel with hot water to prevent funnel from cracking.

5. The filtrate should be faintly yellow. On cooling, a crystalline precipitate forms, mainly cystin, with some tyrosin and leucin. If this is not the case, or if the precipitate is slight, the solution must be concentrated. Save the filtrate, which with the filtrate from 6 is to be worked up later for tyrosin and leucin.

6. After standing overnight filter off the precipitate.

7. Dissolve this precipitate in 350 c.c. of hot 10 per cent. NH_4OH (hood) and let cool. Then continue the cooling with finely chopped ice or with snow. Filter off any tyrosin that may have precipitated, and combine it with the filtrate of 6.

8. Add glacial acetic acid, being careful not to acidify. The precipitate is a mixture of tyrosin and cystin. Filter.

9. Make filtrate from 8 quite acid with glacial acetic acid. The precipitate is almost pure cystin. Let stand twenty-four hours. Then filter, and wash with H_2O and alcohol.

* Lea's Chemical Basis of the Animal Body.

10. Recrystallize by redissolving in as little hot 10 per cent. ammonia as is necessary to effect solution, cooling and precipitating with glacial acetic acid.

The preparations should be pure and contain no tyrosin, for which test may be made with Millon's reagent.

Reactions. — Put a trace of cystin into a test-tube with some dilute NaOH and a little lead acetate. Boil. H_2S is formed because S is split off.

Tyrosin. — 1. Concentrate the neutralized filtrate of 6 of cystin preparation till, on cooling, tyrosin crystallizes out.

2. Filter, and save filtrate for the preparation of leucin.

3. Dissolve the tyrosin crystals in very little hot water.

4. Add amyl alcohol till a heavy precipitate forms.

5. Filter precipitate.

6. Redissolve in very little hot water, and let crystallize out by cooling.

Examine crystals under the microscope.

Test with Millon's reagent.

Leucin. — 1. Take the filtrate of 2 in the preparation of tyrosin, and evaporate to dryness on the water bath.

2. Extract with alcohol.

3. On standing, the leucin crystallizes out of the alcoholic extract as it evaporates.

4. Filter, and dry the crystals.

Examine under the microscope.

Gelatin. — Take about 10 grams of bone, preferably small pieces of the shaft of a long bone, clean carefully, and allow to stand for a few days in 60 c.c. of dilute HCl (1/20). The dilute acid dissolves the inorganic portion of the bone, leaving the collagen. Note the effervescence due to the presence of carbonates. The acid solution is poured off and kept for further investigation. The remains of the bone are allowed to stand overnight in a dilute solution (1/10) of Na_2CO_3, and then boiled in 100 c.c. of water for an hour or two. The collagen undergoes

hydrolysis and is converted into gelatin, which dissolves. A core of bone untouched by the acid usually remains. Evaporate the solution to 25 c.c. bulk and allow to cool. A firm jelly is formed if the solution is sufficiently concentrated. If the solution gelatinizes, add an equal bulk of water and heat anew. If the solution thus obtained is sufficient in quantity it may be used for experiments 208 and 209.

Gelatin may also be prepared from tendons which consist almost wholly of white fibers. Collagen is the substance of which white fibers are made up.

Glycogen $(C_6H_{10}O_5)_n$. — Use a liver taken from an animal just killed, or, if the season permits, oysters just removed from the shell. Cut an oyster, as rapidly as possible, into small pieces, and throw it into four times its weight of boiling water, slightly acidulated with acetic acid. After boiling the first portion for a short time, remove the pieces, grind in a mortar with some sand, return to the water, and continue the boiling for several minutes. Filter while hot. The opalescent solution thus obtained is an aqueous solution of glycogen and other substances.

If a purer solution is desired, continue as follows: Add to the filtrate alternately a few drops of hydrochloric acid and potassio-mercuric iodide, until a precipitate of protein ceases to form. This may be determined more conveniently by filtering off a small portion of the liquid from time to time, and adding to the clear filtrate the hydrochloric acid and potassiomercuric iodide. When the precipitation of the proteins is complete, filter, and to the milky filtrate add double its volume of alcohol; the glycogen will precipitate as a white powder. Filter this off, wash with sixty-six per cent. alcohol (one part of water to two of alcohol), and dissolve in water.

Mucin Solution. — Cut a portion of a navel-cord into small pieces. Shake in a flask with water, changing the water several times. This removes salts and albumin. Extract for twenty-four hours with lime-water or baryta-water in a corked flask.

Filter.   To filtrate add acetic acid, which precipitates the mucin.
Let settle, filter, and wash with water.

Mucin may also be prepared from the saliva by precipitation
with acetic acid.

Potassium Cyanate (KCNO). — Melt in an iron ladle, of at
least 50 c.c. capacity, five grams of commercial potassium cyanide,
and stir in gradually twenty grams of litharge.   When the entire
amount has been added, pour the mass out upon an iron plate,
and allow to cool.   Separate as far as possible the reduced lead
from the potassium cyanate that has been formed, powder the
latter, and dissolve in 25 c.c. of cold water.   Filter if necessary
and purify by repeated crystallization.

Tyrosin. — See paragraph under Cystin, page 432.

Urea, Synthesis of. — Add to a filtered solution of KCNO
a cold saturated solution of ammonium sulphate, containing
at least six grams of $(NH)_2SO_4$.   Heat the mixture slowly on a
water bath at a temperature of 60° C., and maintain at that
point for one hour.   By this process ammonium cyanate is
formed and then changed to urea, which may be obtained in an
impure state by evaporating the solution to dryness on a water
bath, and extracting the residue with hot, strong alcohol.   The
urea will crystallize from the alcohol as it cools.

Vegetable Globulin: e.g. Edestin.   Extract about one ounce
of crushed hemp seed with water containing about 5% sodium
chloride.   This extraction should take from one-half hour to one
hour at a temperature of about 60° C.   Filter while hot.   Upon
cooling, a portion of the globulin (edestin) will probably separate
out.   Use the clear separated fluid for the general protein
reactions and precipitates.   Boil the cloudy portion until the
precipitated globulin has dissolved.   Then set aside for twenty-
four hours that the edestin may crystallize slowly, when hexag-
onal plates should be obtained.   Examine by the microscope.
(See Plate VII, Fig. 1, page 287.)
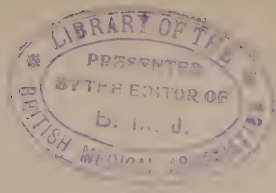
INDEX

A.

Absolute temperature, 13
Acetaldehyde, 208
Acetamide, 235
  preparation (Exp. 123), 393
Acetanilide, preparation of, 249
  test for, 229
Acetates, 100
Acetic acid, 217
  (N/10) factor, 151
  test for (acetates), 100
  volumetric determination of, 151
  anhydride, 218
  ether, 215
Acetone, 210
  bodies, 224
  chloroform, 176
  exp. with, 387
  in blood, 210
  in saliva, 300
    determination of, 313
  in urine, 350
  Legal's test for, 350
  preparation of (Exp. 90), 387
Acetylene, 202
  preparation of (Exp. 67), 382
Acetyl chloride, 218
  salicylic acid, 250
  urea, 239
Achroodextrin, 263
Acid (defined), 4
  albumin, 276
  albuminate, 276
  ammonium urate, 355
  groups, 93
  lactates in urine, 355
  metaprotein, 284
    preparation of (Exp. 224), 410
  phosphates in urine, 355
  potassium oxalate, 221
  protein, 275
  salts, 4
  urates (ammonium and sodium), 355
Acidimetry, 149
Acids of group I, tests for, 93
  of group II, tests for, 95
  of group III, tests for, 98
  of group IV, tests for, 100

Acids, reactions of, 91
Acoin, 173
Acrylic acid, 219
  series, 219
Acrylic aldehyde, 219
Activators, 258
Addition products, 199
Adenin, 241
Adjacent hydrocarbons, 245
Adnephrine, 174
Adrenalin, 174
  chloride, 174
Adrenol, 174
Aich's metal, 114
Alabaster, 71
Albumin in saliva, 298
  test for (Heller's), 314
  in urine, detection of, 343
    Esbach's test, 345
    heat test, 344
    nitric acid test, 344
Albuminoids, 273, 277
Albuminoscope, 344
Albumins, 272, 275
  tests for, 407
Albumose (Exp. 225), 411
Albumoses, 285
Alcohol, 206
  amyl, 207
  butyl, 207
  ethyl, 207
  grain, 207
  methyl, 207
  propyl, 207
  separation of water from (Exp. 76), 384
Alcoholates, 205
Alcoholic fermentation in milk, 284
Alcohols, 205
  atomicity of, 206
  classification of, 206
  exp. with, 384
  oxidation of, 208
Aldehyde, 208
  acetic, 208
  acrylic, 219
  benzoic, 250
  formic, 179, 208

435

Metallic cement, Fletcher's, 30
Metalloids, 16
Metals, classification, 15, 16
    extraction of, 15
    group I, etc. (*see* Group)
    occurrence of, 15
    properties of, 111, 112
    melting-points of, 111
Metaphosphate cement, 135
Metaprotein, 284
    (defined), 274
    preparation of, 410
Metastannic acid, 40
Methane, 197, 200
Methethyl, 181
Methyl-alcohol, 206
    test for, 385
    -amine, 234
    -benzene, 245
    bromide, 203
    carbamine, 229
    carbinol, 207
    chloride, 182, 203
    chloroform, 203
Methylene chloride, 203
    ether, 212
Methyl ether, 212
    ethyl ether, 212
    hydrazine, 235
    indol, 234
    iodide, 203
    orange, 148
    oxide, 212
    salicylate, 250
    urea, 239
Metric equivalents, 12
Michaels, Dr. J. P., albumin in saliva,
    Ref., 298
Michaels, Dr. J. P., methods of saliva
    analysis, Ref., 305
Microchemical analysis, 168
Microchemical methods, 169, 170
Microscosmic salt, 87
Microscope, use of, 168
Milk, 281
    alcoholic fermentation, 284
    experiments with, 409
    fat, 284
    modified, 283
    of magnesia, titration of, 152
    plasma, 281
    reaction of, 281, 282
    specific gravity of, 281
    solids by calculation, 281
    wine, 284

Miller, Dr. W. D., mucin in saliva, Ref.,
    298
Millon's reagent, preparation of, 428
    test (protein), 405
Mineral oil, 199
Mineral salts, metabolism, 366
Minium, 23
Mixed ether, 211
Modified milk, 283
Mohr's method of determination of
    arsenic, 157
Moisture in teeth and tartar, 191
Molar solution (defined), 144
Molecules (defined), 2
Molisch's reagent, 429
Molisch's test for carbohydrates, 400
Monobrom-methane, 203
Monochlor-methane, 178
Monosaccharides, 259
Monoses, 260
Monsel's salt, 54
Morphine, 182
    (Pl. III, Fig. 6), 171
    (microchemical test), 171, 172
    and Marme's reagent (Pl. IV, Fig. 1),
        172
Mosaic gold, 115
Moth scales (Pl. IX, Fig. 6), 353
Mucic acid, 298
Mucin, 280
    experiments with, 410
        (Pl. IX, Fig. 5), 353
    from navel cord, 433
    in saliva, 297
    in urine, 358
Mucoids, 274
Murexide, note, 242
    test, uric acid (Exp. 131), 394
Muscle, 289
    experiments with, 415
    plasma, 289
    serum, 289
Musculin, 415
Myogen, 415
Myogenfibrin, 415
Myosin, 289
    (Exp. 243c), 415
Myosinfibrin, 415
Myosinogen, 289, 415

N.

Naphtha, 200
Natrium, 81
Nephelometer, 296
Nessler's reagent, 29, 429

TABLE OF ATOMIC WEIGHTS (1917)

Aluminium	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton (radium emanation)	Nt	222.4
Bismuth	Bi	208.0	Nitrogen	N	14.01
Boron	B	11.0	Osmium	Os	190.9
Bromine	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.40	Palladium	Pd	106.7
Caesium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.005	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.9
Chlorine	Cl	35.46	Radium	Ra	226.0
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.1	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.4
Dysprosium	Dy	162.5	Scandium	Sc	44.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.3
Fluorine	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	23.00
Gallium	Ga	69.9	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulfur	S	32.06
Glucinium	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	4.00	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.4
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	118.7
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.2
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.20	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium (Neoytterbium)	Yb	173.5
Lutecium	Lu	175.0	Yttrium	Yt	88.7
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6			